Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

Mines Branch

METHODS FOR THE ANALYSIS OF ORES, ROCKS AND RELATED MATERIALS

ELSIE M. DONALDSON

MINES BRANCH MONOGRAPH 881

Available by mail from Information Canada, Ottawa, K1A 0S9
and at the following Information Canada bookshops:

HALIFAX
1683 Barrington Street

MONTREAL
640 St. Catherine Street West

OTTAWA
171 Slater Street

TORONTO
221 Yonge Street

WINNIPEG
393 Portage Avenue

VANCOUVER
800 Granville Street

or through your bookseller

Price: $5.00 Catalogue No. M32-881

Price subject to change without notice

Information Canada
Ottawa, 1974

METHODS FOR THE ANALYSIS OF ORES, ROCKS AND RELATED MATERIALS

Compiled by
ELSIE M. DONALDSON

INORGANIC ANALYTICAL
RESEARCH SECTION
MINERAL SCIENCES DIVISION

MINES BRANCH MONOGRAPH 881

Mines Branch
Department of Energy, Mines and Resources

PREFACE

Since the compilation, in 1958, of a laboratory manual entitled "Methods of Analysis of Ores, Concentrates, and Metallurgical Products used at the Mines Branch Laboratories" (Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Internal Report MDT-58-13) by W.L. Chase, there have been many changes in the nature of methods employed in the Analytical Chemistry Section of the Mineral Sciences Division. Many new instrumental methods have been developed and, in the intervening years, many of the instrumental, gravimetric, and volumetric methods described in the earlier manual have been modified and improved through experience and practice.

Changes have also occurred in the function of the Analytical Chemistry Section. There is now a heavy involvement in the certification of standard reference materials prepared by the Ores Task Force of the Canadian Certified Reference Materials Project (CCRMP) and, for this work, the selection of methods is more critical than for purely routine analysis. Also, the Section is frequently requested by industrial and commercial laboratories (some of which also participate in the CCRM Project) to provide information on methods of analysis for mineralogical and metallurgical materials. However, accounts of many of the new instrumental methods that have been developed or modified in the Section have not been published in the open literature or in Mineral Sciences Division reports and, consequently, have not been available in a form that can be readily disseminated.

For the above reasons the preparation of this new and "up-dated" laboratory manual was considered necessary. Although the manual has been prepared primarily for use within the Mineral Sciences Division, it is expected that it will be of value to chemists in laboratories both within and outside the government. Provisions have been made to make it available to such parties, at a nominal price, through Information Canada.

This manual is intended to provide not only a relatively comprehensive account of the procedures employed for the analysis of each element, but also to furnish novice chemists and other laboratory workers with information on the chemical reactions involved, the interferences to which they are subject, and the limitations of the method. Because some laboratories may not have the instruments or facilities required for some of the newer instrumental methods, many conventional gravimetric and volumetric methods have been included in this manual. Many of these methods are employed in the Analytical Chemistry Section for the determination of "macro" amounts of elements, and for ascertaining the validity of results obtained by instrumental methods. Also included are gravimetric and volumetric methods for the determination of elements that either cannot be determined, or cannot be determined readily by instrumental methods. Particular care has been taken to set forth the steps of each procedure in a logical sequence. An endeavour has also been made to clarify the reason for each step in order to emphasize the importance of details of certain procedures, which, if omitted, could lead to incorrect results. No claim is made for the originality of most of the methods, or that they will be applicable to all types of sample materials encountered, particularly diverse ores and mill products. Furthermore, some of the methods have not been employed for the analysis of all of the related and possible sample materials mentioned. References that provide more detailed information about the individual methods, their applications, and the separation procedures described have been included at the end of the accounts of each method.

With the exception of methods based on combustion techniques, the analytical work of the Analytical Chemistry Section involves only "wet-chemical" procedures. Therefore, instrumental methods based on emission spectroscopy, X-ray fluorescence, neutron-activation analysis, and similar techniques are not included in this manual. Fire-assay methods for the determination of the platinum-group metals by the tin-collection scheme are not included because the detailed procedures have been published in a readily available analytical journal (see "The Tin-Collection Scheme for the Determination of the Platinum-Group Metals, Gold, and Silver", by G.H. Faye and P.E. Moloughney, Talanta, 19, pp 269-284, 1972). Also, the classical fire-assay methods for gold and silver have not been included because of their highly specialized nature, and because they have been fully described by F.E. Beamish in a recent book entitled "The Analytical Chemistry of the Noble Metals" (Pergamon Press, New York, 1966).

ACKNOWLEDGEMENTS

In writing this manual, information has been gathered from many sources and an endeavour has been made to acknowledge the work of others in appropriate references. The classic works "Applied Inorganic Chemistry" by Hillebrand, Lundell, Bright, and Hoffman, "Scott's Standard Methods of Chemical Analysis" by Furman, "Treatise on Analytical Chemistry" by Kolthoff and Elving, "Colorimetric Determination of Traces of Metals" by Sandell, and "Atomic Absorption Spectroscopy" by Slavin were consulted freely in the preparation of accounts of certain procedures, and for information for explanatory notes and on matters pertaining to interferences. Maxwell's "Rock and Mineral Analysis", and the above-mentioned work by Hillebrand et al have been particularly valuable in the preparation of accounts of procedures for the analysis of silicate minerals and of silicate and carbonate rocks. Within the Analytical Chemistry and the Inorganic Analytical Research Sections, special thanks are due to R.C. McAdam, Chief Chemist of the Analytical Chemistry Section, J.C. Hole, Leader of the Metallic Ores and Non-Metallic Minerals Group, G.H. Faye, Leader of the

Inorganic Analytical Research Group, and to the following members of the above sections for thir helpful comments and suggestions: D.J. Charette, R.R. Craig, C.H. McMaster, R.S. Kobus, P. Lanthier, R.G. Sabourin, and B. Nebesar. Personal acknowledgements are due to Mr. V.A. Haw, former Chief of the Mineral Sciences Division, Dr. R.L. Cunningham, present Chief, and Dr. John Convey, former Director of the Mines Branch for permitting me to devote my time to this project; to G.H. Faye and Dr. N.F.H. Bright for their critical review of this manual; to Mrs. A. Purdy,Mrs. D.M. Varette, and Mrs. V. McDiarmid for typing the original and master drafts of the methods; and to D. Lister for preparing the final illustrations.

FORMAT OF THE MANUAL AND PRESENTATION OF THE METHODS

Because most chemists and other laboratory workers, particularly those engaged in the analysis of ores and mill products, are in need of rapid, routine instrumental methods of analysis, this manual has been organized so that the first three of its five sections describe instrumental methods, and the last two describe conventional gravimetric and volumetric methods. With the exception of Part I, which involves atomic-absorption spectrophotometric and flame-emission photometric methods, the methods have been listed alphabetically according to the elements being determined. This was not possible in Part I without producing needless repetition in written accounts of the decomposition and sample preparation procedures.

In Part I and also in Part III, which involves polarographic methods of analysis, the directions given for the preparation of standard calibration solutions are, of necessity, very general, and the lower range given for the method is only approximate because of the extreme differences in the sensitivities of commercial atomic-absorption spectrophotometers and polarographs. When using these methods, particularly those involving atomic-absorption spectrophotometry and flame-emission photometry, some preliminary work should be conducted to determine the appropriate instrumental conditions, and the approximate sensitivity of and range for the element in question. Standard calibration solutions should subsequently be prepared accordingly. In atomic-absorption spectrophotometry and flame-emission photometry, calibration solutions that give a linear response when absorbance or emission values are plotted against concentration should be employed whenever possible. When necessary, sensitivity can be reduced by using a less sensitive absorption or emission line for the desired element. Unless specific directions are given for the preparation of blank calibration solutions, pure water should be em-employed to calibrate the zero absorbance or emission setting of the instrument.

In Parts II, IV, and V, which involve light-absorption spectrophotometric, gravimentric, and volumetric methods of analysis, respectively, needless repetition in the written accounts of sample decomposition, and particularly, of separation procedures has been avoided (e.g., in cases in which one or more elements are determined in the filtrate remaining after the separation of the element in question) by referring subsequent procedures back to the appropriate sample decomposition and/or prior separation step.

The concentrations of ammonium hydroxide and all concentrated acids employed in the methods are those shown in Table I in the Appendix. Unless otherwise stated, distilled or de-mineralized water should be employed for the preparation of dilute solutions of the above reagents. Unless specific directions are given for the preparation of solutions of solid reagents, all such solutions should be made with distilled water.

In the instructions for preparing calibration graphs in Part II, which involves light-absorption spectrophotometric methods, the specified conditions (i.e., volume and cell size) have been chosen to provide a convenient range of absorbance values. In all of the methods described in this section, the exact recommended volume of the solution of the complex-forming or chromogenic reagent should be added to the calibration and sample solutions.

Ottawa, Canada
December 1973

Elsie M. Donaldson

CONTENTS

PART I

ATOMIC-ABSORPTION SPECTROPHOTOMETRIC AND FLAME-EMISSION PHOTOMETRIC METHODS

PART II

LIGHT-ABSORPTION SPECTROPHOTOMETRIC METHODS

PART III

POLAROGRAPHIC METHODS

PART IV

GRAVIMETRIC METHODS

PART V

VOLUMETRIC METHODS

APPENDIX

PART I

ATOMIC-ABSORPTION SPECTROPHOTOMETRIC AND FLAME-EMISSION PHOTOMETRIC METHODS

DETERMINATION OF ALUMINUM, CALCIUM, MAGNESIUM, AND IRON IN ACID-SOLUBLE SILICATE ROCKS AND MINERALS, SILICA SAND, QUARTZITE, SANDSTONE, CLAY, AND SHALE

Principle

Aluminum, calcium, and magnesium are determined by atomic-absorption spectrophotometry, at 309.3, 422.7, and 285.2 nm, respectively, in a nitrous oxide-acetylene flame, after the addition of a solution of high potassium content to both the sample and the standard calibration solutions[1,2]. Iron is determined in a similar manner, at 248.3 nm, in a slightly oxidizing air-acetylene flame.

Outline

The sample is decomposed with hydrofluoric, hydrochloric, and perchloric acids. The solution is evaporated to near dryness to remove silica and excess acids, and the salts are dissolved in dilute hydrochloric acid. The resulting solution is analyzed for aluminum, calcium, magnesium, and iron.

Discussion of interferences

Interference from aluminum, which suppresses both calcium and magnesium absorption in low-temperature (air-acetylene) flames because of the formation of stable aluminates, is avoided by using the high-temperature nitrous oxide-acetylene flame for the determination of calcium and magnesium[3,4]. Alkali metals (sodium, potassium, and cesium) enhance calcium, magnesium, and aluminum absorption in the high-temperature nitrous oxide-acetylene flame because of decreased ionization of these elements[1,2,4-6] and, if present in large amounts, they slightly suppress iron absorption in the air-acetylene flame[7]. Interference from the alkali metals, particularly in the determination of calcium, magnesium, and aluminum, is minimized by the addition of identical amounts of a solution of high potassium content to both the sample and the standard calibration solutions[1,2].

Interference from hydrochloric acid, which particularly influences aluminum absorption in the nitrous oxide-acetylene flame[8], is compensated for by maintaining approximately the same hydrochloric acid concentration (2% by volume) in the sample and standard calibration solutions. Moderate amounts of other elements that may be present in silicate rocks and other siliceous materials do not interfere in the determination of calcium, magnesium, and iron[1,2]. However, titanium enhances aluminum absorption in the nitrous oxide-acetylene flame[9,10]. The magnitude of this effect depends on flame conditions (i.e., oxidant-fuel ratio, and height of the optical path above the burner). Interference from titanium can be essentially eliminated by measuring the aluminum absorbance approximately 15 mm above the burner in a fuel-rich flame[10].

Range

The method is suitable for silica sand, quartzite, and sandstone samples containing more than approximately 0.02% of aluminum, and more than 0.005% of calcium, magnesium, and iron. It is suitable for silicate rock and mineral, clay, and shale samples containing up to approximately 10% of each element, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard aluminum solution, 500 ppm. Dissolve 0.5000 g of high-purity aluminum metal by heating gently with 25 ml of concentrated hydrochloric acid. Cool, and dilute to 1 litre with water.

Standard calcium solution, 500 ppm. Transfer 1.2487 g of calcium carbonate (dried at 125°C for 1-2 hours) to a 400-ml beaker, add approximately 200 ml of water, then cover the beaker and add 10 ml of concentrated hydrochloric acid in small portions. When the decomposition of the carbonate is complete, boil the solution gently to expel carbon dioxide, cool to room temperature, transfer to a 1-litre volumetric flask, and dilute to volume with water. Prepare a 50-ppm solution by diluting 20 ml of this stock solution to 200 ml with water.

Standard magnesium solution, 500 ppm. Decompose 0.5000 g of high-purity magnesium metal by the method described above for the preparation of the standard calcium solution. Cool the resulting solution to room temperature, transfer it to a 1-litre volumetric flask, and dilute to volume with water. Prepare a 20-ppm solution by diluting 10 ml of this stock solution to 250 ml with water.

Standard iron solution, 500 ppm. Dissolve 0.5000 g of high-purity iron metal by heating gently with 20 ml of concentrated hydrochloric acid. Cool, and dilute to 1 litre with water. Prepare a 50-ppm solution as described above.

Potassium solution, 20,000 ppm. Dissolve 19.07 g of potassium chloride in water, and dilute to 500 ml.

Hydrochloric acid, 50% v/v.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add 2 ml of concentrated hydrochloric acid and 5 ml of the 20,000-ppm potassium solution; then, by burette, add suitable varying increments of the standard 500-ppm aluminum solution. Add 2 ml of concentrated hydrochloric acid and 5 ml of the potassium solution to a separate flask; this constitutes the blank calibration solution. Dilute each solution to volume with water and mix.

Prepare, in a similar manner, a suitable series of standard calcium, magnesium, and iron solutions using the dilute standard 50-, 20-, and 50-ppm solutions, respectively.

Procedures

In these procedures a reagent blank is carried along with the samples.

Silica sand, quartzite, and sandstone

Transfer 0.5-3 g of powdered sample, depending on the expected content of the element or elements to be determined (Note 1), to a 100-ml platinum dish and, depending on the amount of sample taken, add 10-20 ml of concentrated hydrofluoric acid. Allow the mixture to digest at room temperature for approximately 30 minutes, then add 10 ml each of concentrated hydrochloric and perchloric acids, and evaporate the resulting solution to fumes of perchloric acid. Cool, and add 10 ml each of water and concentrated hydrofluoric and hydrochloric acids. Evaporate the solution to fumes again and, if necessary, repeat the addition of hydrofluoric and hydrochloric acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water, evaporate the solution to fumes, then repeat the washing and evaporation steps to ensure the complete removal of hydrofluoric acid, and evaporate the solution until approximately 1.5 ml of perchloric acid remain (Note 2). Add 10 ml of water and 4 ml of 50% hydrochloric acid, and heat gently until the solution becomes clear (Note 3). Cool, transfer the solution to a 100-ml volumetric flask, dilute to volume with water and mix (Note 4).

Transfer suitable aliquots (up to 50 ml) of the resulting sample solution, and a 50-ml aliquot of the blank solution (Note 5) to separate 100-ml volumetric flasks. Add 5 ml of the 20,000-ppm potassium solution, and sufficient 50% hydrochloric acid so that approximately 2 ml of concentrated hydrochloric acid are present, dilute to volume with water and mix. Measure the aluminum, calcium, and/or magnesium absorbances of the resulting solutions at 309.3, 422.7, and 285.2 nm, respectively, in a nitrous oxide-acetylene flame. Measure the iron absorbance in a slightly oxidizing air-acetylene flame at 248.3 nm. Determine the content of the desired element or elements in the blank and sample aliquots by relating the resulting values to those obtained concurrently for standard solutions of slightly higher and lower concentrations. Correct the final aluminum, calcium, magnesium, and/or iron results obtained for the sample solution by subtracting those obtained for the reagent blank solution.

Silicate rocks and minerals, clay, and shale

Decompose 0.5 g of powdered sample by the method described above. Evaporate the solution to fumes of perchloric acid 2 or 3 times to ensure the complete removal of hydrofluoric acid, then evaporate the solution until approximately 3 ml of perchloric acid remain. Cool, add 20 ml of 50% hydrochloric acid and heat gently until the solution becomes clear (Note 3). Transfer the solution to a 500-ml volumetric flask, dilute to volume with water, mix (Notes 4 and 6), and proceed with the determination of aluminum, calcium, magnesium, and/or iron as described above.

Notes

1. The calcium and magnesium contents of silica sand and sandstone are usually greater than the aluminum and iron contents. Furthermore, the sensitivity of the determination of calcium, and particularly of magnesium by atomic-absorption spectrophotometry is considerably greater than that of aluminum and iron. Consequently, if only calcium and/or magnesium are to be determined in the above materials, a moderately small amount of sample (0.5-1 g) should be taken to avoid excessive dilution of the subsequent sample solution.

2. If aluminum is to be determined, the sample solution should not be evaporated to dryness at this stage. This results in the formation of anhydrous aluminum compounds, which are virtually insoluble in water or dilute acid, and causes low results for aluminum[11].

3. If any acid-insoluble material is present, it should be removed by filtration, ignited at about 750°C in a platinum crucible, and fused with approximately 0.5 g of sodium carbonate. The cooled melt should subsequently be dissolved in the initial solution.

4. If acid-insoluble material has not been treated as described in Note 3, the sample solution can be used for the determination of sodium and potassium by the Radiation Buffer Method (p 27), and also for the determination of lithium by the Basic Lead Carbonate Method (p 21), after removal of excess hydrochloric and perchloric acids from a suitable aliquot or aliquots of the solution by evaporation.

5. For the most accurate determination of the aluminum, calcium, magnesium, and/or iron contents of the reagent blank solution, the largest possible aliquot should be employed for subsequent measurement.

6. If the sample contains an appreciable amount of titanium, any insoluble titanium compounds that are formed by hydrolysis during dilution of the sample solution can be removed by filtering a suitable portion of the solution through a dry filter paper (Whatman No. 42).

Calculations

$\%Al_2O_3 = 1.890 \times \%\ Al$

$\%\ CaO = 1.399 \times \%\ Ca$

$\%MgO = 1.658 \times \%\ Mg$

$\%Fe_2O_3 = 1.430 \times \%\ Fe$

Other applications

This method can be employed to determine aluminum, calcium, magnesium, and iron in glass and asbestos. It can also be used to determine iron, calcium, and/or magnesium in gypsum, fluorspar, dolomite, limestone, and cement.

References

1. F.J. Langmyhr and P.E. Paus, Anal. Chim. Acta, 43, 397 (1968).

2. W. Slavin, "Atomic Absorption Spectroscopy", Interscience, New York, pp 78-79, 87-94, 125-128, 244 (1968).

3. M.D. Amos and J.B. Willis, Spectrochim. Acta, 22, 1325 (1966).

4. R.W. Nesbitt, Anal. Chim. Acta, 35, 413 (1966).

5. D.C. Manning and L. Capacho-Delgado, ibid., 36, 312 (1966).

6. P.E. Paus, ibid., <u>54</u>, 164 (1971).

7. R. Höhn and F. Umland, Z. Anal. Chem., <u>258</u>, 100 (1972).

8. P. König, K.-H. Schmitz and E. Thiemann, Atomic Absorption Newsletter, <u>9</u>, 103 (1970); Z. Anal. Chem., <u>244</u>, 232 (1969).

9. T.V. Ramakrishna, P.W. West and J.W. Robinson, Anal. Chim. Acta, <u>39</u>, 81 (1967).

10. J.Y. Marks and G.G. Welcher, Anal. Chem., <u>42</u>, 1033 (1970).

11. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. <u>4</u>, 377 (1966).

DETERMINATION OF ALUMINUM, CALCIUM, AND MAGNESIUM IN IRON ORES AND CONCENTRATES

Principle

Aluminum, calcium, and magnesium are determined by atomic-absorption spectrophotometry, at 396.2, 422.7, and 285.2 nm, respectively, in a nitrous oxide-acetylene flame, by comparison with standard calibration solutions containing approximately the same amounts of the matrix element and acid as the sample solution[1].

Outline

The sample is decomposed with hydrochloric and nitric acids, and the solution is evaporated to dryness to remove excess acids. The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate and the melt is dissolved in the initial filtrate. The resulting solution is analyzed for aluminum, calcium, and magnesium.

Discussion of interferences

Interference from hydrochloric acid and large amounts of iron, which influence aluminum absorption in a nitrous oxide-acetylene flame[2], is compensated for by simulating the composition of the sample in the standard solutions employed for calibration purposes.

Interference from aluminum, which suppresses both calcium and magnesium absorption in low-temperature (air-acetylene) flames due to the formation of stable aluminates, is avoided by using the high-temperature nitrous oxide-acetylene flame for the determination of calcium and magnesium[3,4]. Moderate amounts of phosphorus do not interfere in the determination of calcium and magnesium in the nitrous oxide-acetylene flame[5].

Moderate amounts of titanium, phosphorus, and other elements that are normally present in iron ores (e.g., chromium, manganese, and vanadium) do not cause significant error in the aluminum result when the aluminum absorbance is measured approximately 15 mm above the burner in a fuel-rich flame[6].

Range

The method is suitable for samples containing approximately 0.2 to 10% of aluminum, 0.02 to 10% of calcium, and 0.02 to 5% of magnesium.

Reagents

Standard aluminum, calcium, and magnesium solutions, 500, 50, and 20 ppm, respectively. Prepare as described in the method for silicate rocks (pp 3 and 4).

Synthetic matrix solution A. Dissolve 12 g of high-purity iron metal (aluminum-, calcium-, and magnesium-free) by heating gently with 60 ml of concentrated hydrochloric acid. Add sufficient concentrated nitric acid, by drops, to oxidize any ferrous iron present, and evaporate the solution to a paste. Add 120 ml of concentrated hydrochloric acid, warm gently to dissolve the paste, and dilute the solution to approximately 500 ml with water. Add 22 g of sodium chloride, and stir to dissolve. Transfer the resulting solution to a 2-litre volumetric flask, and dilute to volume with water (Notes 1 and 2).

Synthetic matrix solution B. Transfer 500 ml of matrix solution A to a 2-litre volumetric flask, add 90 ml of concentrated hydrochloric acid (Note 3), and dilute to volume with water.

Hydrochloric acid, 10% v/v.

Sulphuric acid, 50% v/v.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add 50 ml of synthetic matrix solution A; then, by burette, add suitable varying increments of the standard 500-ppm aluminum solution. Add 50 ml of the matrix solution to a separate flask; this constitutes the blank calibration solution. Dilute each solution to volume with water and mix.

Prepare, in a similar manner, a blank calibration solution, and a suitable series of combined calcium and magnesium solutions, using the dilute standard 50- and 20-ppm solutions, and 50 ml of synthetic matrix solution B.

Procedure

In this procedure a reagent blank, prepared by decomposing 1.2 g of high-purity iron metal as described, is carried along with the samples (Note 4).

Transfer 2 g of powdered sample to a 250-ml beaker, and moisten with several ml of water. Add 30 ml of concentrated hydrochloric acid, cover the beaker, and heat gently, without boiling, until the decomposition of acid-soluble material is complete. Add 4 ml of concentrated nitric acid, boil gently for several minutes, remove the cover, and evaporate the solution to dryness. Add 10 ml of concentrated hydrochloric acid to the residue, cover, and warm gently for several minutes. Add approximately 50 ml of water, and heat the solution to the boiling point. Filter the resulting solution (Whatman No. 40 paper) into a 250-ml beaker, and transfer the residue quantitatively to the filter paper. Wash the beaker, paper, and residue three times with 20-, 20-, and 10-ml portions of 10% hydrochloric acid (Note 5), then thoroughly with hot water until the paper is free of ferric chloride.

Transfer the paper and residue to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at 850°C. Cool the crucible, and add 1 ml of 50% sulphuric acid and 5-10 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid. Add 2 g of sodium carbonate to the residue, cover the crucible, and fuse the mixture over a blast burner until a clear melt is obtained. Cool, and transfer the crucible and cover to the beaker (covered) containing the initial filtrate. When the dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with water. If necessary (Note 6), filter the resulting solution (Whatman No. 42 paper) into a 200-ml volumetric flask, dilute to volume with water and mix.

To determine aluminum, transfer a 5-50-ml aliquot of both the blank and sample solutions, depending on the expected aluminum content of the sample, to 100-ml volumetric flasks. If necessary, dilute to exactly 50 ml with synthetic matrix solution A (Note 7), then dilute to volume with water and mix. Measure the absorbance of the resulting solutions, at 396.2 nm, in a nitrous oxide-acetylene flame. Determine the aluminum content of the blank and sample aliquots by relating the resulting values to those obtained concurrently for standard aluminum solutions of slightly higher and lower concentrations. Correct the final result obtained for the sample solution by subtracting that obtained for the reagent blank solution.

To determine calcium and magnesium, transfer 25-ml aliquots of both the initial blank and sample solutions to 100-ml volumetric flasks, add 4.5 ml of concentrated hydrochloric acid (Note 8), dilute to volume with water and mix. Transfer a 2-50-ml aliquot or aliquots of both solutions, depending on the expected calcium and magnesium contents of the sample, to 100-ml volumetric flasks. If necessary, dilute to exactly 50 ml with synthetic matrix solution B (Note 7), then dilute to volume with water and mix. Measure the calcium and magnesium absorbances of the resulting solutions, at 422.7 and 285.2 nm, respectively, in a nitrous oxide-acetylene flame. Determine the calcium and magnesium contents of the blank and sample aliquots, as described above, by comparison with absorbance values obtained for standard solutions of slightly higher and lower concentrations. Correct the final calcium and magnesium results obtained for the sample solution by subtracting those obtained for the reagent blank solution.

Notes

1. The iron content of the synthetic matrix solutions (A and B) is based on ores containing 60% of iron. However, the standard calibration solutions, prepared by using 50-ml portions of these solutions, can be employed for

the analysis of samples containing considerably lesser or greater amounts of iron (±20%) without producing appreciable error in the aluminum, calcium, or magnesium results.

2. The amount of sodium chloride used in the preparation of the synthetic matrix solution compensates (i.e., in the resulting standard calibration solutions) for the amount of sodium ion contributed to the sample solution by the sodium carbonate employed for fusion of the acid-insoluble residue.

3. The hydrochloric acid concentration of the synthetic matrix solutions (A and B) is maintained at approximately 6% by volume, so that the final concentration of acid in the resulting calibration solutions will be approximately 3% by volume after dilution of 50-ml portions to 100 ml with water.

4. The high-purity iron metal used for the reagent blank should be the same as that initially employed for the preparation of the synthetic matrix solution.

5. Only the approximate recommended amounts of 10% hydrochloric acid should be employed for washing purposes so that the concentration of hydrochloric acid in the resultant sample solution will be approximately 6% by volume (Note 3) after dissolution of the subsequent sodium carbonate melt and dilution of the solution to 200 ml with water (2 g of sodium carbonate react with approximately 3.2 ml of concentrated hydrochloric acid).

6. If the sample contains an appreciable amount of titanium, the solution may be turbid because of the presence of insoluble titanium compounds formed by hydrolysis.

7. By diluting small aliquots of the sample and blank solutions to 50 ml with the synthetic matrix solution, the iron and acid contents of the resulting solutions will be approximately the same as those of the standard calibration solutions, prepared by using 50-ml portions of the synthetic matrix solution (Notes 3 and 5). Consequently, the calibration solutions can be employed for the subsequent analysis, regardless of the size of the aliquot taken.

8. The recommended amount of hydrochloric acid is added so that the resultant acid concentration of the solution will be approximately 6% by volume after dilution to volume with water.

Calculations

$\%Al_2O_3 = 1.890 \times \%\ Al$

$\%CaO = 1.399 \times \%\ Ca$

$\%MgO = 1.658 \times \%\ Mg$

References

1. Technical Committee 102 - Iron Ores, "Determination of Aluminum, Calcium, and Magnesium in Iron Ores by Atomic Absorption", International Organization for Standardization, Document 218E, November (1970).
2. P. König, K.-H. Schmitz and E. Thiemann, Atomic Absorption Newsletter, 9, 103 (1970); Z. Anal. Chem., 244, 232 (1969).
3. M.D. Amos and J.B. Willis, Spectrochim. Acta, 22, 1325 (1966).
4. R.W. Nesbitt, Anal. Chim. Acta, 35, 413 (1966).
5. D.C. Manning and L. Capacho-Delgado, ibid., 36, 312 (1966).
6. J.Y. Marks and G.G. Welcher, Anal. Chem., 42, 1033 (1970).

DETERMINATION OF BARIUM, CALCIUM, AND MAGNESIUM IN STRONTIUM-BEARING MINERALS, ORES AND MILL PRODUCTS, AND DETERMINATION OF STRONTIUM, CALCIUM, AND MAGNESIUM IN BARIUM-BEARING MINERALS, ORES AND MILL PRODUCTS

Principle

This method is based on the conversion of insoluble barium and strontium sulphates to carbonates, and subsequent conversion of the insoluble carbonates to soluble chlorides[1]. Barium is determined by emission flame-photometry, using the standard-additions method, at 553.6 nm, in a nitrous oxide-acetylene flame, after the addition of a solution of high potassium content to both the sample and the standard calibration solutions[2]. Strontium, and also calcium and magnesium, which are also converted to carbonates and subsequently to chlorides, are determined in a similar manner, by atomic-absorption spectrophotometry, at 460.7, 422.7, and 285.2 nm, respectively, in the same flame[2,3].

Outline

The sample is decomposed by fusion with sodium carbonate to convert barium and strontium sulphates, and calcium and magnesium to their carbonates. The melt is digested in water, and the insoluble carbonates of these elements are separated from sulphate and various other elements (phosphorus, aluminum, alkali metals, and some silica) by filtration. After dissolution of the precipitate, residual silica is removed from the solution by volatilization as silicon tetrafluoride. Iron, if present in large amounts, is removed by a mercury cathode separation. The resulting solution, or the preceding solution, if large amounts of iron are absent, is ultimately analyzed for calcium and magnesium and, depending on the nature of the sample, for either barium or strontium.

Discussion of interferences

Small amounts of barium, calcium, and magnesium enhance strontium absorption in the low-temperature air-acetylene flame because of decreased ionization of the strontium. Large amounts of barium and magnesium suppress strontium absorption, presumably because of the formation in the flame of refractory compounds which remove strontium atoms[4,5]. Calcium strongly enhances barium emission and absorption in an air-acetylene flame because of intense CaOH bands that peak at the barium resonance line[2,6,7]. These interference effects are reduced by using the high-temperature nitrous oxide-acetylene flame.

Other possible mutual interference effects, particularly that of large amounts of barium or strontium on the absorption of calcium and magnesium, and that of large amounts of strontium on the emission of barium are minimized by using the standard-additions method for the determination of magnesium and the alkaline earth elements[2,6,8,9].

Interference from large amounts of iron, which influence strontium absorption in the nitrous oxide-acetylene flame, is avoided by removing this element by a mercury cathode separation. Interference from perchloric and hydrochloric acids, which also influence strontium absorption in the above flame, is eliminated by evaporating the subsequent sample solution to dryness. The addition of identical amounts of a solution of high potassium content to both the sample and the standard calibration solutions enhances calcium, magnesium, and strontium absorption, and also barium emission because of the resultant decrease in the ionization of these elements in the high-temperature nitrous oxide-acetylene flame[2-5,8,9].

Range

The method is suitable for samples containing approximately 0.02 to 10% of barium and strontium, 0.01 to 4% of calcium, and 0.005 to 2% of magnesium. Material containing higher concentrations of these elements can also be analyzed with reasonable accuracy.

Apparatus

Mercury cathode.

Reagents

Standard barium solution, 500 ppm. Transfer 0.7184 g of pure barium carbonate (dried at 125°C for 1-2 hours) to a 400-ml beaker, add approximately 200 ml of water, then cover the beaker and add 4 ml of concentrated hydrochloric acid in small portions. When the decomposition of the carbonate is complete, boil the solution gently to expel carbon dioxide, cool to room temperature, transfer to a 1-litre volumetric flask, and dilute to volume with water. Prepare a 100-ppm solution by diluting 50 ml of this stock solution to 250 ml with water.

Standard strontium solution, 500 ppm. Decompose 0.8424 g of pure strontium carbonate (dried at 125°C for 1-2 hours) by the method described above for the preparation of the standard barium solution. Transfer the resulting solution to a 1-litre volumetric flask, and dilute to volume with water. Prepare a 100-ppm solution as described above.

Standard calcium and magnesium solutions, 50, and 20 ppm respectively. Prepare as described in the method for silicate rocks (pp 3 and 4).

Potassium solution, 20,000 ppm. Prepare as described in the method for silicate rocks (p 4).

Barium chloride solution, 10% w/v. Dissolve 10 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in water, and dilute to 100 ml.

Sodium carbonate wash solution, 1% w/v.

Hydrochloric acid, 30% v/v.

Preparation of standard calibration solutions

Depending on the expected barium, calcium, magnesium, and/or strontium contents of the sample solution (prepared as described below), add aliquots of the sample solution identical to the aliquot taken for the determination of the desired element, to two 100-ml volumetric flasks. By burette, add suitable increments of the dilute standard solution of the desired element (Note 1) and 5 ml of the 20,000-ppm potassium solution to each flask, dilute to volume with water and mix.

Procedure

In this procedure a reagent blank is carried along with the samples only if calcium and/or magnesium are to be determined (Note 2).

Transfer 0.5 g of powdered sample (Notes 3 and 4) to a 30-ml platinum crucible, add 5 g of sodium carbonate and mix thoroughly. Cover the crucible, and fuse the mixture over a blast burner for approximately 30 minutes (Note 5). Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, and allow the crucible and contents to cool. Transfer the crucible and cover to a 400-ml Teflon beaker, and add approximately 200 ml of water. Heat gently to disintegrate the melt, then remove the crucible and cover after washing them thoroughly with hot water. Filter the resulting solution (Whatman No. 40 paper) and wash the paper and precipitate at least 12 times with hot 1% sodium carbonate solution to ensure the complete removal of sulphate ion (Note 6). Discard the filtrate and washings.

Using a jet of hot water, transfer the bulk of the precipitate to the Teflon beaker, and cover the beaker with a watch glass. Dissolve the small amount of precipitate remaining on the filter paper, using hot 30% hydrochloric acid, and wash the paper thoroughly with hot water. Collect the resulting solution in the beaker containing the precipitate. If necessary, add sufficient concentrated hydrochloric acid to dissolve the precipitate, then remove the cover, add 5 ml of concentrated hydrofluoric acid and 10 ml of concentrated perchloric acid, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and again evaporate the solution to fumes. Repeat the washing and evaporation steps to ensure the complete removal of hydrofluoric acid, then evaporate the solution until approximately 5 ml of perchloric acid remain. Cool, add approximately 50 ml of water, and heat gently until the solution becomes clear (Note 7). Cool, transfer the solution to a mercury cathode cell, dilute to about 250 ml with water, and electrolyze the solution for 30 minutes at approximately 10 amperes. Filter the electrolyte (Whatman No. 541 paper) into a 400-ml pyrex beaker, evaporate it to complete dryness, then add approximately 50 ml of water and 2-3 drops of concentrated hydrochloric acid, and heat gently to dissolve the salts. Cool, transfer the solution to a 100-ml volumetric flask, dilute to volume with water and mix.

Transfer suitable aliquots (up to 50 ml) of the sample solution, depending on the expected content of the element or elements to be determined, and a 50-ml aliquot of the blank solution (Note 8), to separate 100-ml volumetric flasks. Add 5 ml of the 20,000-ppm potassium solution, dilute to volume with water and mix. Measure the strontium (i.e., in solutions derived from barium-bearing minerals, ores, and mill products), calcium, and/or magnesium absorbances of the resulting solutions, at 460.7, 422.7, and 285.2 nm, respectively, in a nitrous oxide-acetylene flame (Note 9), and determine the content of the desired element or elements in the sample aliquots by the standard-additions method (Note 1). Measure the barium emission (i.e., in solutions derived from strontium-bearing minerals, ores, and mill products), at 553.6 nm, in a nitrous oxide-acetylene flame (Note 10), and determine the barium content of the aliquot in a similar manner. Correct the final calcium and magnesium results obtained for the sample solution by subtracting those obtained for the reagent blank solution.

Notes

1. In the standard-additions method, the known amount of the desired element that is added to one of the sample aliquots should be of the same order of magnitude as the amount of the element already present in the aliquot. Because this method for determining the concentration of the unknown element in the sample solution is valid only if the relationship between absorbance (or emission) and concentration is linear, the preparation and measurement of a second calibration solution, containing a different amount of the dilute standard solution of the desired element, is essential. This procedure provides a duplicate analysis and confirms the linearity of the above relationship. In the subsequent analysis, the amount, or concentration "C" of the desired element in the aliquot or diluted solution taken for analysis can be calculated from the following equation:

$$\frac{C}{C + a} = \frac{A_1}{A_2} \quad \text{or} \quad C = \frac{A_1 \times a}{A_2 - A_1}$$

where:

a = the known amount (mg or µg) of the element added to the sample aliquot, or the resultant concentration (ppm) of the added element in the diluted solution.

A_1 = the absorbance (or emission) of the diluted sample solution containing "C" units of the unknown desired element.

A_2 = the absorbance (or emission) of the diluted sample solution containing "C + a" units of the desired element.

2. The water and the reagents employed in this method do not normally contain barium or strontium.

3. If the sample contains organic material, it should be ignited at 800-900°C for approximately 30 minutes, prior to fusion with sodium carbonate[1].

4. In the absence of sulphates, relatively pure strontianite ($SrCO_3$), witherite ($BaCO_3$), and baryto-calcite ($BaCO_3.CaCO_3$) can be decomposed with hydrochloric acid, followed by evaporation of the solution to dryness to remove the excess acid and to dehydrate any silica present[1]. Depending upon the nature of the sample, calcium, magnesium, and either barium or strontium can be determined by the standard-additions method, as described in the subsequent procedure, after dissolution of the residue in hot water containing several drops of concentrated hydrochloric acid, and filtration of the resulting solution to remove silica. If calcium is to be determined in baryto-calcite samples, further dilution of the initial sample solution will be required.

5. The fusion should be started with a low flame which is gradually raised to the full heat of the burner. This precaution is necessary to prevent loss by overflowing.

6. Complete removal of sulphate ion is indicated when the addition of 10% barium chloride solution to the washings, after acidification of the

washings with hydrochloric acid, no longer yields a white precipitate of barium sulphate.

7. If the sample contains only small amounts of iron (i.e., ores and concentrates), as indicated by the bulk and colour of the initial precipitate, the subsequent mercury cathode separation of iron can be omitted. In this case, transfer the solution to a 250-ml pyrex beaker, evaporate it to complete dryness, then proceed as described.

8. For the most accurate determination of the calcium and magnesium contents of the reagent blank solution, the largest possible aliquot should be employed for subsequent measurement (Note 9).

9. The standard-additions method cannot be employed to determine the calcium and magnesium contents of the reagent blank solution. These can be determined, in the usual manner, by relating the resulting absorbance values to those obtained concurrently for a blank calibration solution, and appropriate standard calcium and magnesium solutions of slightly higher concentrations, containing an identical amount of the 20,000-ppm potassium solution.

10. Barium can be determined by atomic-absorption spectrophotometry, if desired, but the flame-emission method is more sensitive[2,8].

Calculations

%BaO = 1.116 x % Ba

%CaO = 1.399 x % Ca

%MgO = 1.658 x % Mg

%SrO = 1.183 x % Sr

$\%BaSO_4$ = 1.699 x % Ba

$\%CaSO_4$ = 3.397 x % Ca

$\%MgSO_4$ = 4.950 x % Mg

$\%SrSO_4$ = 2.096 x % Sr

$\%BaCO_3$ = 1.437 x % Ba

$\%CaCO_3$ = 2.497 x % Ca

$\%MgCO_3$ = 3.468 x % Mg

$\%SrCO_3$ = 1.685 x % Sr

Other applications

This method can be employed to determine barium and strontium in silicate rocks and minerals.

References

1. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 139-140 (1962).
2. S.R. Koirtyohann and E.E. Pickett, Spectrochim. Acta, 23B, 673 (1968).
3. D.C. Manning and L. Capacho-Delgado, Anal. Chim. Acta, 36,312 (1966).
4. W. Slavin, "Atomic Absorption Spectroscopy", Interscience, New York, pp 164-171 (1968).
5. R. Intonti and A. Stacchini, Spectrochim. Acta, 23B, 437 (1968).
6. L. Capacho-Delgado and S. Sprague, Atomic Absorption Newsletter, 4, 363 (1965).
7. S.R. Koirtyohann and E.E. Pickett, Anal. Chem., 38, 585 (1966).
8. J.D. Kerber and W.B. Barnett, Atomic Absorption Newsletter, 8, 113 (1969).
9. M.D. Amos and J.B. Willis, Spectrochim. Acta., 22, 1325 (1966).

DETERMINATION OF COPPER, NICKEL, ZINC, COBALT, CADMIUM AND IRON IN SULPHIDE MINERALS, ORES AND MILL PRODUCTS

Principle

Copper, nickel, zinc, cobalt, cadmium, and iron are determined, in a dilute nitric acid solution of the sample, by atomic-absorption spectrophotometry, at 324.8, 232.0, 213.9, 240.7, 228.8, and 248.3 nm, respectively, in an air-acetylene flame.

Outline

The sample is decomposed with hydrochloric, nitric, hydrofluoric, and perchloric acids, and the solution is evaporated to a paste to remove silica and excess acids. The paste is dissolved in dilute nitric acid, and acid-insoluble material is removed by filtration. The resulting filtrate is analyzed for copper, nickel, zinc, cobalt, cadmium and, depending on the amount of copper, nickel, and cobalt present, for iron.

To determine iron in samples containing large amounts of copper, nickel, and/or cobalt, the sample is decomposed with hydrochloric, nitric, and perchloric acids. Silica is dehydrated by evaporation and ultimately removed by filtration. The acid-insoluble material is ignited, and silica is removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate, and the melt is dissolved in the initial filtrate. Iron is precipitated as the hydrous oxide with ammonium hydroxide, and separated from copper, nickel, cobalt, and various other elements (cadmium, zinc, and manganese) by filtration. The precipitate is dissolved in dilute nitric acid, and the resulting solution is analyzed for iron.

Discussion of interferences

Moderate amounts of cations, anions, and nitric acid do not interfere in the determination of copper, nickel, zinc, cobalt, and cadmium in an air-acetylene flame[1]. Large amounts of iron (1000 ppm or more) slightly enhance cobalt and nickel absorption, but up to approximately 2500 ppm do not interfere in the determination of copper. Copper, nickel, and cobalt seriously depress iron absorption[2-4]. The magnitude of these effects is strongly dependent on the flame conditions (i.e., fuel-to-air ratio, and height of the optical path above the burner), and on the acid or anion present in the sample solution[2]. Interference from the above elements is eliminated by separating iron from these elements by precipitation as the hydrous oxide with ammonium hydroxide. Small amounts of copper, nickel, and cobalt (equal to, or less than the amount of iron present), nitric acid at concentrations up to 5% by volume, and up to approximately 5000 ppm of chromium, manganese, zinc, cadmium, magnesium, and aluminum do not cause significant error in the iron result[2].

Range

Procedure A is suitable for samples containing approximately 0.02 to 5% of copper, nickel, zinc, cobalt, cadmium, and iron. Procedure B is suitable for samples containing approximately 0.2 to 5% of iron. Material containing higher concentrations of these elements can be analyzed with reasonable accuracy by both procedures.

Reagents

Standard copper, nickel, zinc, cobalt, cadmium, and iron solutions, 1000 ppm. Dissolve 0.5000 g of high-purity foil or granules of each of the metals by heating gently with 20 ml of 50% nitric acid. Cool, and dilute each solution to 500 ml with water. Prepare 50-ppm solutions by diluting 25 ml of each stock solution to 500 ml with water.

Sulphuric acid, 50% v/v.

Nitric acid, 20%, 5%, and 2% v/v.

Hydrochloric acid wash solution, 2% v/v.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add 2 ml of concentrated nitric acid; then, depending on the element to be determined, add, by burette, suitable varying increments of the respective dilute standard 50-ppm solution. Add 2 ml of concentrated nitric acid to a separate flask; this constitutes the blank calibration solution. Dilute each solution to volume with water and mix.

Procedures

In these procedures a reagent blank is carried along with the samples only if small amounts of copper, zinc, and/or iron are to be determined (Note 1).

A - General procedure

Transfer 0.1-0.5 g of powdered sample (Note 2), depending on the expected content of the element or elements to be determined, to a 400-ml Teflon beaker. Add 10 ml of concentrated hydrochloric acid, cover the beaker with a Teflon cover, and boil for several minutes. Add 10 ml of concentrated nitric acid, boil until most of the sulphide minerals are decomposed, then add 5 ml of concentrated hydrofluoric acid and 10 ml of concentrated perchloric acid. Boil the solution for several minutes, remove the cover, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and evaporate the solution to a moist paste. Cool, add 3 ml of concentrated nitric acid and approximately 25 ml of water, and heat to dissolve the soluble salts. Add some dry paper pulp to the solution, filter it (Whatman No. 40 paper) into a 250-ml volumetric flask, and wash the beaker, paper and residue with 40 ml of warm 5% nitric acid followed by hot water (Note 3). Cool the filtrate to room temperature, dilute to volume with water and mix.

Measure the copper, nickel, zinc, cobalt, cadmium, and/or iron (Note 4) absorbances of the resulting blank and sample solutions, or suitable aliquots diluted to appropriate volumes with 2% nitric acid, at 324.8, 232.0, 213.9, 240.7, 228.8, and 248.3 nm, respectively, in an air-acetylene flame. Determine the content of the desired element or elements, in the solutions or aliquots, by relating the resulting values to those obtained concurrently for standard solutions of slightly higher and lower concentrations. If necessary, (Note 1), correct the final copper, zinc, and/or iron results obtained for the sample solution by subtracting those obtained for the reagent blank solution.

B - Procedure for the determination of iron in samples containing large amounts of copper, nickel, and/or cobalt

Transfer 0.1-2.5 g of powdered sample, containing at least 5 mg of iron, to a 400-ml pyrex beaker, add 20 ml of concentrated hydrochloric acid, cover the beaker, and boil for several minutes. Add 20 ml of concentrated nitric acid, boil until most of the sulphide minerals are decomposed, then add 10 ml of concentrated perchloric acid. Boil the solution for several minutes, remove the cover, and evaporate the solution to a moist paste. Cool, add 10 ml of concentrated hydrochloric acid, warm gently for several minutes, then add approximately 50 ml of water, and heat the solution to the boiling point. Filter the resulting solution (Whatman No. 40 paper) into a 400-ml beaker, wash the beaker, paper, and residue with warm 2% hydrochloric acid until the paper is free of ferric chloride, then with hot water (Note 5).

Transfer the paper and residue to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 750°C. Cool the crucible, and add 1 ml of 50% sulphuric acid and 3-5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid. Fuse the residue with 1 g of sodium carbonate (or potassium pyrosulphate); cool, and transfer the crucible and contents to the beaker (covered) containing the initial filtrate. When the dissolution of the melt is complete, remove the crucible after washing it thoroughly with hot water, and dilute the resulting solution to approximately 150 ml with water.

Neutralize the solution approximately with concentrated ammonium hydroxide to precipitate the hydrous oxide of iron, add approximately 5 ml in excess and boil the solution for several minutes to coagulate the precipitate. Allow the precipitate to settle, then filter the solution (Whatman No. 541 paper) and wash the beaker, paper, and precipitate thoroughly with hot water to remove ammonia and ammonium salts. Discard the filtrate and washings. Dissolve the precipitate, using approximately 40 ml of warm 20% nitric acid, and wash the paper thoroughly with 40 ml of warm 5% nitric acid followed by hot water. Collect the resulting solution in the beaker in which the precipitation was carried out, and discard the paper. Cool the filtrate to room temperature, transfer it to a 500-ml volumetric flask, dilute to volume with water, mix, and proceed with the determination of iron as described above.

Notes

1. The water and the reagents employed do not normally contain nickel, cobalt, or cadmium. A reagent blank is not necessary if these elements or large amounts of copper, zinc, and/or iron are to be determined.

2. This procedure is not applicable to molybdenum and tungsten sulphide minerals, ores, and mill products.

3. If the acid-insoluble material is suspected to contain any of the elements to be determined, proceed as follows:

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at 750°C. Fuse the residue with approximately 1 g of sodium carbonate, cool, and transfer the crucible and contents to a 250-ml beaker (covered) containing 50 ml of water and 2 ml of concentrated nitric acid. When the dissolution of the melt is complete, remove the crucible after washing it thoroughly with water, and add the solution to the initial solution. After dilution of the combined solution to volume with water, the resulting sample solution, or suitable aliquots diluted to appropriate volumes with 2% nitric acid, can be analyzed for the desired element or elements by the standard-additions method to compensate for matrix depressant effects resulting from the high sodium salt concentration[5].

4. If the copper, nickel, and/or cobalt contents of the sample are greater than the iron content, Procedure B should be employed for the determination of iron.

5. If only the acid-soluble iron content of the sample is required, discard the residue, and proceed as described.

References

1. W. Slavin, "Atomic Absorption Spectroscopy", Interscience, New York, pp 86-87, 100-104, 136, 186 (1968).
2. J.M. Ottaway, D.T. Coker, W.B. Rowston and D.R. Bhattarai, Analyst, 95, 567 (1970).
3. A.F. Cunningham, Atomic Absorption Newsletter, 8, 70 (1969).
4. J.L. Carper, ibid., 9, 48 (1970).
5. R. Höhn and F. Umland, Z. Anal. Chem., 258, 100 (1972).

DETERMINATION OF LEAD IN SULPHIDE ORES AND MILL PRODUCTS

Principle

Lead is determined by atomic-absorption spectrophotometry, at 217.0 nm, in a slightly oxidizing air-acetylene flame, after separation from sulphate by precipitation as the mixed hydrous oxide and carbonate[1], and subsequent conversion to soluble lead nitrate.

Outline

The sample is decomposed with hydrochloric, nitric, and perchloric acids, and acid-soluble lead is ultimately precipitated as the hydrous oxide, in a slightly ammoniacal medium, by occlusion with hydrous ferric oxide. Acid-insoluble lead sulphate, initially present in the sample, and/or formed during the decomposition procedure, is converted to lead carbonate by the subsequent addition of ammonium carbonate. Lead is separated from the resultant ammonium sulphate by filtration of the mixed hydrous oxide-lead carbonate precipitate. The precipitate is dissolved in nitric acid and insoluble material is removed by filtration. The resulting filtrate is analyzed for lead.

Discussion of interferences

Moderate amounts of cations and anions, with the exception of those that form insoluble lead compounds (e.g., sulphate), do not interfere in the determination of lead in an air-acetylene flame[2].

Range

The method is suitable for samples containing approximately 0.02 to 10% of lead, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard lead solution, 1000 ppm. Dissolve 0.5000 g of pure lead foil by heating gently with 20 ml of 50% nitric acid. Cool, and dilute to 500 ml with water. Prepare a 100-ppm solution by diluting 25 ml of this stock solution to 250 ml with water.

Iron (III) solution, 3% w/v. Dissolve 3 g of high-purity iron metal (lead-free) in 20 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, cool, and dilute the solution to 100 ml with water.

Ammonium carbonate solution, saturated.

Nitric acid wash solution, 10 % v/v.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add 2 ml of concentrated nitric acid; then, by burette, add suitable varying increments of the dilute standard 100-ppm lead solution. Dilute each solution to volume with water and mix.

Procedure

Transfer 0.1-0.5 g of powdered sample, containing up to approximately 10 mg of lead (Note 1), to a 400-ml beaker, add 10 ml of concentrated hydrochloric acid, cover the beaker, and boil for several minutes. Add 10 ml of concentrated nitric acid, boil until most of the sulphide minerals are decomposed, then add 10 ml of concentrated perchloric acid. Boil the solution for several minutes, remove the cover, and allow the solution to evaporate to a paste. Add 10 ml of concentrated nitric acid and approximately 20 ml of water, and heat to dissolve the soluble salts (Note 2).

Dilute the solution to approximately 150 ml with water and, if necessary, add sufficient 3% iron(III) solution so that the iron content of the solution is at least 20 times that of the lead. Add sufficient concentrated ammonium hydroxide to precipitate hydrous ferric oxide, then add several drops in excess, followed by 15 ml of saturated ammonium carbonate solution. Boil the resulting solution for several minutes to coagulate the precipitate, then filter the solution (Whatman No. 541 paper), and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the filtrate and washings.

Using a jet of hot water, transfer the bulk of the precipitate to the original beaker, add 10 ml of concentrated nitric acid, and heat gently to dissolve the precipitate. Filter the solution through the original filter paper into a volumetric flask of appropriate size (200-1000 ml), and wash the paper and residue alternately with warm 10% nitric acid and hot water. Discard the paper and residue. Cool the filtrate to room temperature, dilute to volume with water and mix.

Measure the absorbance of the resulting solution, or a suitable aliquot diluted to an appropriate volume with water, at 217.0 nm, in a slightly oxidizing air-acetylene flame. Determine the lead content of the solution or aliquot by relating the resulting value to those obtained concurrently for standard lead solutions of slightly higher and lower concentrations.

Notes

1. Samples containing more than approximately 10 mg of lead are not recommended because of the bulkiness of the subsequent mixed hydrous oxide-lead carbonate precipitate.

2. Any insoluble material (i.e., silicates) that is present at this stage may be ignored because it is removed by filtration during the subsequent procedure.

References

1. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, 503, 516 (1939).

2. W. Slavin and D.C. Manning, Appl. Spectry., 19, 65 (1965).

DETERMINATION OF LITHIUM IN LITHIUM ORES AND MILL PRODUCTS, ACID-SOLUBLE SILICATE ROCKS AND MINERALS, QUARTZITE, SANDSTONE, SILICA SAND, CLAY, AND SHALE BY THE BASIC LEAD CARBONATE METHOD

Principle

This method[1] is a modification of that developed by Ellestad and Horstman[2], and involves the separation of certain matrix elements from lithium by precipitation with basic lead carbonate from a dilute sulphuric acid medium. Lithium is determined either by atomic-absorption spectrophotometry or by emission flame-photometry, at 670.8 nm, in a slightly oxidizing air-acetylene flame.

Outline

The sample is decomposed with perchloric, hydrochloric, hydrofluoric, and sulphuric acids, and the solution is evaporated to dryness to remove silica and excess acids. The salts are dissolved in dilute sulphuric acid, and iron, aluminum, calcium, and phosphate are precipitated by the addition of solid basic lead carbonate, and separated from lithium by filtration. The resulting filtrate is ultimately analyzed for lithium.

Discussion of interferences

Matrix elements, which suppress lithium absorption[3], and particularly lithium emission[1,2], if present in large amounts, are separated from lithium by precipitation with basic lead carbonate. Sodium, potassium, and magnesium are not separated from lithium by this procedure, but up to approximately 500 ppm of these elements do not interfere in the determination of lithium by atomic-absorption spectrophotometry[3,4].

Radiation or ionization interference from sodium and potassium, in the determination of lithium by emission flame-photometry, is minimized by the addition of identical amounts of a solution of high sodium and potassium content to both the sample and the standard lithium calibration solutions[1]. Up to approximately 400 ppm of magnesium do not interfere in the determination of lithium by emission flame-photometry[2].

Range

The method is suitable for samples containing more than approximately 0.001% of lithium.

Reagents

Standard lithium solution, 1000 ppm. Transfer 2.6621 g of lithium carbonate (dried at 125°C for 1-2 hours) (Note 1) to a 400-ml beaker, add approximately 200 ml of water, then cover the beaker and add 6.5 ml of concentrated hydrochloric acid in small portions. When the decomposition of the carbonate is complete, boil the solution gently to expel carbon dioxide, cool to room temperature, transfer to a 500-ml volumetric flask, and dilute to volume with water. Prepare a 100-ppm solution by diluting 50 ml of this stock solution to 500 ml with water.

Radiation buffer solution, 25,000 ppm of sodium and potassium. Dissolve 31.8 g of sodium chloride and 23.9 g of potassium chloride in water, and dilute to 500 ml (Note 2).

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Sulphuric acid, 50% and 10% v/v.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add, by burette, suitable varying increments of the dilute standard 100-ppm lithium solution. If lithium is to be determined by emission flame-photometry, add 2 ml of radiation buffer solution to each flask, and to a separate 100-ml flask; this constitutes the blank calibration solution. Dilute each solution to volume with water and mix.

Procedure

Transfer 0.2-0.5 g of powdered sample, depending on the expected lithium content, to a 100-ml platinum dish, add 5 ml of concentrated perchloric acid (Note 3), mix, and evaporate the mixture to dryness. Add 5 ml each of 50% sulphuric acid and concentrated hydrochloric and hydrofluoric acids, and evaporate the solution to fumes of sulphur trioxide. Cool, add 5 ml each of water and concentrated hydrofluoric and hydrochloric acids. Evaporate the solution to fumes again and, if necessary, repeat the addition of water and the above acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water, and evaporate the solution to complete dryness. Cool, add approximately 25 ml of water and 1 ml of 10% sulphuric acid (Note 4), and heat gently to dissolve the salts. Transfer the solution to a 250-ml beaker, dilute to approximately 75 ml with water, and add several drops of 0.1% methyl red solution. Cover the beaker, heat the solution to the boiling point, and add solid basic lead carbonate, in small portions, until the solution is alkaline to methyl red (i.e., lemon-yellow in colour). Boil the resulting solution for several minutes, filter it (Whatman No. 42 paper) into a 250-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hot water. Add 5 ml of 50% sulphuric acid to the filtrate to precipitate any remaining lead, and evaporate the solution to dryness (Note 5). Cool, wash down the sides of the beaker with water, and again evaporate the solution to dryness. Add approximately 25 ml of water to the residue, boil the solution for about 5 minutes, filter it (Whatman No. 42 paper) into a volumetric flask of appropriate size (100-1000 ml) (Note 6), dilute to volume with water and mix.

If lithium is to be determined by atomic-absorption spectrophotometry, measure the absorbance of the resulting solution, or a suitable aliquot diluted to an appropriate volume with water, at 670.8 nm, in a slightly oxidizing air-acetylene flame. Determine the lithium content of the solution or aliquot by relating the resulting value to those obtained concurrently for standard lithium solutions of slightly higher and lower concentrations.

If lithium is to be determined by emission flame-photometry, transfer a 5-50-ml aliquot of the solution to a 100-ml volumetric flask, add 2 ml of radiation buffer solution (Note 7), dilute to volume with water and mix. Measure the emission of the solution, at 670.8 nm, in an air-acetylene flame, and determine the lithium content of the aliquot as described above, but by comparison with emission values obtained for standard lithium solutions containing an identical amount of radiation buffer solution.

Notes

1. If lithium carbonate is not available, the standard solution can be prepared by dissolving 4.6095 g of lithium sulphate monohydrate ($Li_2SO_4 \cdot H_2O$) in water, and diluting the solution to 500 ml.

2. The radiation buffer solution is not required if lithium is to be determined by atomic-absorption spectrophotometry.

3. If the sample contains carbonates, moisten it with approximately 10 ml of water, cover, and add the perchloric acid in small portions. When the decomposition of the carbonates is complete, proceed as described.

4. If the sample contains an appreciable amount of phosphate (e.g., amblygonite), add 5 ml of 10% sulphuric acid at this stage to ensure the complete dissolution of lithium phosphate. After dilution of the solution and addition of methyl red, neutralize the solution approximately with concentrated ammonium hydroxide, then add 1 ml of 10% sulphuric acid and proceed as described.

5. If ammonium hydroxide has been employed to neutralize excess acid (Note 4), evaporate the solution to approximately 50 ml, then cover, and add 15 ml of concentrated nitric acid and 5 ml of concentrated hydrochloric acid to decompose the resultant ammonium salts, prior to evaporation of the solution to dryness.

6. If the lithium content of the sample is expected to be very low, and lithium is to be determined by emission flame-photometry, filter the sample solution into a 100-ml volumetric flask, add 2 ml of radiation buffer solution, dilute to volume with water, and proceed as described.

7. Alternatively, compensation can be made for ionization interference from sodium and potassium by determining the approximate sodium and potassium contents of the final or diluted sample solution, and then adding the equivalent amounts to the lithium calibration solutions[2].

Calculations

$$\%Li_2O = 2.153 \times \%\ Li$$

Other applications

This method can be employed to determine lithium in glass and ceramic materials (e.g., flint clay and firebrick).

References

1. Elsie M. Penner (Donaldson) and W.R. Inman, "Flame Photometric Methods used in the Mineral Sciences Division", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB24, September (1961).

2. R.B. Ellestad and E.L. Horstman, Anal. Chem., 27, 1229 (1955).

3. S. Abbey, "Analysis of Rocks and Minerals by Atomic-Absorption Spectroscopy - Part 1. Determination of Magnesium, Lithium, Zinc and Iron", Dept. of Energy, Mines and Resources, Geological Survey of Canada, Ottawa, Paper 67-37 (1967).

4. F.Z. Patassy, Plant Soil, 22, 395 (1965).

DETERMINATION OF MANGANESE IN IRON ORES AND MILL PRODUCTS

Principle

Manganese is determined, in a dilute perchloric acid solution of the sample, by atomic-absorption spectrophotometry, at 279.5 nm, in a slightly oxidizing air-acetylene flame.

Outline

The sample is decomposed with hydrochloric, nitric, hydrofluoric, and perchloric acids. The solution is evaporated to fumes of perchloric acid to remove silica and excess hydrofluoric acid, and diluted with water. The resulting solution is analyzed for manganese.

Discussion of interferences

Up to at least 1500 ppm of iron, 3000 ppm of calcium and potassium, 1000 ppm of sodium and magnesium, 500 ppm of phosphorus, and moderate amounts of other elements that may be present in iron ores and mill products (e.g., titanium, chromium, vanadium, and aluminum) do not interfere in the determination of manganese in an air-acetylene flame[1-3]. Perchloric acid, at concentrations up to approximately 10% by volume, does not cause significant error in the manganese result when the absorbance is measured in a lean air-acetylene flame, using a single-slot burner[4].

Range

The method is suitable for samples containing approximately 0.01 to 10% of manganese.

Reagents

Standard manganese solution, 500 ppm. Transfer 0.5000 g of high-purity manganese metal to a 400-ml beaker, cover the beaker, add approximately 30 ml of water and 10 ml of concentrated nitric acid, and heat gently until the decomposition of the metal is complete. Remove the cover, add 10 ml of concentrated perchloric acid, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and again evaporate the solution to fumes. Add approximately 25 ml of water, then add sufficient 3% hydrogen peroxide, by drops, to dissolve any manganese dioxide that may have separated during evaporation of the solution to fumes of perchloric acid, and boil the solution for approximately 5 minutes to remove excess hydrogen peroxide. Cool, transfer the resulting solution to a 1-litre volumetric flask, dilute to volume with water and mix. Prepare a 50-ppm solution by diluting 20 ml of this stock solution to 200 ml with water.

Hydrogen peroxide, 3% w/v.
Dilute 10 ml of 30% hydrogen peroxide to 100 ml with water.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add, by burette, suitable varying increments of the dilute standard 50-ppm manganese solution. Dilute each solution to volume with water and mix.

Procedure

Transfer 0.5 g of powdered sample to a 400-ml Teflon beaker, add 15 ml of concentrated hydrochloric acid, cover with a Teflon cover, and heat gently, without boiling, for approximately 30 minutes. Remove the cover, add 15 ml of water, 10 ml of concentrated perchloric acid, and 5 ml each of concentrated nitric and hydrofluoric acids, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and evaporate the solution until approximately 5 ml of perchloric acid remain. Add approximately 50 ml of water, and heat gently to dissolve the salts (Notes 1 and 2). Transfer the solution to a volumetric flask of appropriate size (250-1000 ml), depending on the expected manganese content, dilute to volume with water (Note 3) and mix.

Measure the absorbance of the resulting solution, or a suitable aliquot diluted to an appropriate volume with water, at 279.5 nm, in a slightly oxidizing air-acetylene flame. Determine the manganese content of the solution or aliquot by relating the resulting value to those obtained concurrently for standard manganese solutions of slightly higher and lower concentrations.

Notes

1. If some manganese has separated as manganese dioxide at this stage, add 2-3 drops of 3% hydrogen peroxide to dissolve the brown dioxide, then boil the solution for approximately 5 minutes to remove excess hydrogen peroxide.

2. If any acid-insoluble material is present, it should be removed by filtration, ignited at about 750°C in a platinum crucible, and fused with approximately 0.5 g of sodium carbonate. The resultant cooled melt should be dissolved in the initial solution.

3. If the sample contains an appreciable amount of titanium, any insoluble titanium compounds that are formed by hydrolysis during dilution of the sample solution can be removed by filtering a suitable portion of the solution through a dry filter paper (Whatman No. 42).

Calculations

$$\%MnO = 1.291 \times \%\ Mn$$

Other applications

This method can be employed to determine manganese in silicate rocks and minerals, glass and, probably, in steel.

References

1. C.B. Belcher and K. Kinson, Anal. Chim. Acta, 30, 483 (1964).
2. J.E. Allan, Spectrochim. Acta, 15, 800 (1959).
3. F.J. Langmyhr and P.E. Paus, Anal. Chim. Acta, 43, 397 (1968); 45, 157 (1969).
4. W.B. Barnett, Anal. Chem., 44, 695 (1972).

DETERMINATION OF POTASSIUM AND SODIUM IN ACID-SOLUBLE SILICATE ROCKS AND MINERALS, CLAY, SHALE, AND IRON, COPPER, NICKEL, TITANIUM, MOLYBDENUM, NIOBIUM AND TANTALUM ORES AND MILL PRODUCTS BY THE RADIATION BUFFER METHOD

Principle

Potassium and sodium are determined, either by atomic-absorption spectrophotometry or by emission flame-photometry, at 589.0 and 766.5 nm, respectively, in a slightly oxidizing air-acetylene flame, after the addition of a solution of high iron, aluminum, calcium, and magnesium contents to both the sample and the standard calibration solutions[1].

Outline

Silicate rocks and minerals, clay, and shale, are decomposed with perchloric, hydrochloric, hydrofluoric, and sulphuric acids, and the solution is evaporated to dryness to remove silica and excess acids. The salts are dissolved in dilute hydrochloric acid, and insoluble material is removed by filtration. The resulting filtrate is analyzed for sodium and potassium.

Iron, copper, and nickel ores and mill products are decomposed with hydrochloric, nitric, hydrofluoric, and sulphuric acids. The solution is evaporated to fumes of sulphur trioxide to remove silica and hydrofluoric acid, and iron, copper, and nickel are ultimately separated from sodium and potassium by a mercury cathode separation. Titanium, molybdenum, niobium, and tantalum ores and mill products are decomposed in a similar manner. Titanium and molybdenum are separated by chloroform extraction of their cupferron complexes, and niobium and tantalum are separated by hydrolytic precipitation of their hydrous oxides. The resulting solutions are ultimately analyzed for sodium and potassium.

Discussion of interferences

Interference from matrix elements (iron, aluminum, calcium, and magnesium) that are normally present in silicate rocks, ores, and other materials, and which, if present in large amounts, usually suppress both sodium and potassium emission and absorption[1,2], is minimized by the addition of identical amounts of a solution of high iron, aluminum, calcium, and magnesium contents to both the sample and the standard sodium and potassium calibration solutions. Similar interference from other matrix elements (e.g., iron, copper, nickel, titanium, molybdenum, niobium, and tantalum), present in ore and mill product samples, is avoided by separating these elements from sodium and potassium by the procedures described under "Outline"[1].

Ionization interference from lithium, rubidium, and cesium, and mutual ionization interference from potassium in the determination of sodium and vice versa[1,3-5], is compensated for by adding the approximate amounts of these elements, present in the final sample solution, to the standard calibration solutions.

Range

The method is suitable for samples containing more than approximately 0.01% of sodium and/or potassium.

Reagents

Standard sodium solution, 1000 ppm. Dissolve 1.2709 g of sodium chloride (dried at 125°C for 1-2 hours) in water, and dilute to 500 ml. Dilute 50 ml of this stock solution to 500 ml with water. Store both the stock and the diluted 100-ppm solution in polyethylene bottles (Note 1).

Standard potassium solution, 1000 ppm. Dissolve 0.9534 g of potassium chloride (dried at 125°C for 1-2 hours) in water, and dilute to 500 ml. Prepare a 100-ppm solution as described above, and store both the stock and the diluted solution in polyethylene bottles.

Standard sodium and potassium solution, 100 ppm. Transfer 50-ml aliquots of both the sodium and potassium stock solutions to a 500-ml volumetric flask, dilute to volume with water, and store in a polyethylene bottle.

Radiation buffer solution. Dissolve 86.9 g of aluminum nitrate nonahydrate [Al $(NO_3)_3 \cdot 9H_2O$], 22.6 g of ferric nitrate nonahydrate [Fe $(NO_3)_3 \cdot 9H_2O$], and 22.6 g of magnesium chloride hexahydrate $(MgCl_2 \cdot 6H_2O)$ in approximately 150 ml of water (Note 2). Transfer 7.8 g of calcium carbonate to a 400-ml beaker, add approximately 200 ml of water, then cover the beaker and add 18 ml of concentrated hydrochloric acid in small portions. When the decomposition of the carbonate is complete, boil the solution gently to expel carbon dioxide, and cool to room temperature. Filter both solutions (Whatman No. 541 paper) into a 500-ml volumetric flask, dilute to volume with water, mix, and store in a polyethylene bottle.

Cupferron solution, 9% w/v. Prepare fresh as required, and filter the solution, if necessary.

Sulphuric acid, 50% v/v. Store in a polyethylene bottle.

Chloroform. Analytical reagent-grade.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add 4 ml of the radiation buffer solution; then, by burette, add suitable increments of the dilute standard 100-ppm sodium and potassium solutions, or the combined solution, depending on the approximate sodium and potassium contents of the sample solution to be analyzed (Note 3). Add 4 ml of the radiation buffer solution to a separate flask; this constitutes the blank calibration solution. Dilute each solution to volume with water and mix (Note 4). Prepare fresh as required (Note 5).

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Silicate rocks and minerals, clay, and shale

Transfer 0.25-0.5 g of powdered sample (Note 6), depending on the expected sodium and potassium contents, to a 100-ml platinum dish (Note 7), add 5 ml of concentrated perchloric acid (Note 8), mix, and evaporate the mixture to dryness. Add 5 ml each of 50% sulphuric acid and concentrated hydrochloric and hydrofluoric acids, and evaporate the solution to fumes of sulphur trioxide. Cool, add 5 ml each of water and concentrated hydrofluoric and hydrochloric acids. Evaporate the solution to fumes again and, if necessary, repeat the addition of water and the above acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water, and evaporate the solution to complete dryness. Cool, add approximately 25 ml of water and 3 drops of concentrated hydrochloric acid (Note 9), and heat gently until the solution becomes clear. Transfer the resulting solution (Note 7) to a 400-ml beaker, filter it (Whatman No. 40 paper) (Note 10) into a 250-ml volumetric flask, dilute to volume with water and mix (Notes 11 and 12).

Transfer 5-50-ml aliquots of the sample solution, and a 50-ml aliquot of the blank solution (Note 13) to separate 100-ml volumetric flasks. Add 4 ml of radiation buffer solution, dilute to volume with water and mix. Measure the sodium and potassium absorbances or emissions of the resulting solutions, at 589.0 and 766.5 nm, respectively, in a slightly oxidizing air-acetylene flame. Determine the sodium and potassium contents of the blank and sample aliquots by relating the resulting values to those obtained concurrently for standard sodium and potassium solutions of slightly higher and lower concentrations (Notes 3 and 14). Correct the final sodium and potassium results obtained for the sample solution by subtracting those obtained for the reagent blank solution.

B - Iron, copper, and nickel ores and mill products

Transfer 0.25-0.5 g of powdered sample, depending on the expected sodium and potassium contents, to a 250-ml Teflon beaker, and add 12 ml of 50% sulphuric acid and 5 ml each of concentrated hydrochloric, nitric, and hydrofluoric acids. Cover the beaker with a Teflon cover, heat gently for approximately 15 minutes, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, add 5 ml each of water and concentrated hydrochloric, nitric, and hydrofluoric acids. Evaporate the solution to fumes again and, if necessary, repeat the addition of water and the above acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the beaker with water, and again evaporate the solution to fumes. Repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid. Cool, add approximately 50 ml of water, and heat gently until the solution becomes clear.

Transfer the solution to a mercury cathode cell, dilute to about 250 ml with water, and electrolyze the solution for 1 hour at approximately 10 amperes. Filter the electrolyte (Whatman No. 541 paper) into a 400-ml pyrex beaker, evaporate it to complete dryness, then add approximately 50 ml of water and 3 drops of concentrated hydrochloric acid, and heat gently to dissolve the salts. Filter the resulting solution (Whatman No. 40 paper) into a 250-ml volumetric flask, dilute to volume with water, mix, and proceed with the determination of sodium and potassium as described above.

C - Titanium and molybdenum ores and mill products

Decompose 0.25-0.5 g of sample by the method described in Procedure B, using 22 ml of 50% sulphuric acid rather than 12 ml. Evaporate the solution to fumes of sulphur trioxide 3 or 4 times to ensure the complete removal of hydrofluoric acid, then add approximately 50 ml of water, and heat gently until the solution is clear (Note 15). Transfer the resulting solution to a 500-ml separatory funnel, dilute to approximately 100 ml with water, and cool to about 10°C in an ice-bath. Add sufficient cold 9% cupferron solution (Note 16) to precipitate iron (if present), and titanium or molybdenum, then mix, stopper, and extract the cupferrates by repeated shaking, for 1 minute each time, with two 50-ml and then three or more 25-ml portions of chloroform until the organic layer is colourless (Note 17). Discard each extract.

Transfer the aqueous phase to a 400-ml pyrex beaker, warm gently to remove the residual chloroform, then evaporate the solution to approximately 50 ml. Cover the beaker, add 10 ml each of concentrated nitric and hydrochloric acids, and boil the solution for 20-30 minutes to destroy organic material. Cool, remove the cover, and evaporate the solution to fumes of sulphur trioxide. If organic material is still present, repeat the treatment with nitric and hydrochloric acids, then evaporate the solution to complete dryness. Add approximately 50 ml of water and 3 drops of concentrated hydrochloric acid, and heat gently to dissolve the salts. Filter the solution into a 250-ml volumetric flask, dilute to volume with water, and proceed with the determination of sodium and potassium as described in Procedure A.

D - Niobium and tantalum minerals, ores and mill products

Decompose 0.1-0.2 g of powdered sample (Note 18) by the method described in Procedure B (Note 19), using a 400-ml Teflon beaker. After complete removal of hydrofluoric acid, evaporate the solution until approximately 2-3 ml of sulphuric acid remain (Note 20). Cool, add about 200 ml of water, cover the beaker, and boil the solution for approximately 30 minutes to precipitate the hydrous oxides of niobium and/or tantalum. Filter the hot solution (Whatman No. 42 paper) into a 400-ml pyrex beaker, and wash the beaker, paper, and precipitate thoroughly with hot water (Note 21). Discard the paper and precipitate. Evaporate (Note 22) the filtrate to complete dryness, add about 30 ml of water and 2 drops of concentrated hydrochloric acid, and heat to dissolve the salts. Filter the resulting solution into a 100-ml volumetric flask, dilute to volume with water, and proceed with the determination of sodium and potassium as described in Procedure A.

Notes

1. Standard solutions of sodium and potassium, and other solutions employed in this method should be stored in polyethylene bottles to avoid contamination of the solution by alkali metals, particularly sodium, from glass containers.

2. Reagents with high sodium and potassium contents should not be employed for the preparation of the radiation buffer solution.

3. Because sodium interferes in the determination of potassium and vice versa, both by atomic-absorption spectrophotometry and, particularly by emission flame-photometry, especially in high-temperature flames, standard calibration solutions containing equal amounts of sodium and potassium should be employed only for the analysis of samples that also contain approximately equal amounts (±5 ppm) of both elements. For accurate analysis, a prior estimate of the sodium and potassium contents of the final diluted sample solution should be made, using appropriate standard solutions containing radiation buffer solution and equal amounts of sodium and potassium. Subsequently, suitable standard solutions, in which the equivalent amount of potassium present in the diluted sample solution is added to the standard sodium solutions and vice versa, should be prepared (using the dilute standard sodium and potassium solutions) and employed for the analysis of the sample solution.

4. The approximate concentrations of the radiation buffer elements in the resulting solutions are 500 ppm of aluminum, and 250 ppm each of iron, calcium, and magnesium.

5. The standard solutions should be prepared fresh daily because hydrolysis of iron and aluminum, and contamination of the solutions by alkali metals in the glass occurs on standing.

6. This procedure is applicable to all acid-soluble silicate materials (e.g., granite, feldspar, mica, quartzite, sandstone, silica sand, spodumene, lepidolite, chlorite schist, serpentinite, and nepheline syenite) except those with high phosphorus contents. Samples containing large amounts of phosphorus (e.g., phosphate rock) can be analyzed by the modified J. Lawrence Smith Method (p 33). Pollucite can also be analyzed by Procedure A, provided the rubidium and cesium contents are known and exact additions of these elements are made to the standard calibration solutions[1].

7. To avoid contamination of the subsequent sample solution with sodium from the hands, the platinum dish should be handled at all stages with clean, preferably platinum, tongs.

8. If the sample contains carbonates, moisten it with approximately 10 ml of water, cover, and add the perchloric acid in small portions. When the decomposition of the carbonates is complete, proceed as described.

9. The acid concentration of the sample solution should be minimal because large amounts of acid suppress sodium and potassium absorption and emission[1,3].

10. Filtration of the sample solution is recommended to ensure the complete removal of trace amounts of solid material that may clog the atomizer tube during the subsequent analysis.

11. The resulting solution should preferably be analyzed for sodium and potassium on the same day that it is prepared, to avoid contamination of the solution by alkali metals in the glass (Note 5). If a delay is necessary, transfer the solution to a polyethylene bottle.

12. The sample solution can be used for the determination of calcium and magnesium by atomic-absorption spectrophotometry (p 3), and also for the determination of lithium, either by the above method or by emission flame-photometry, after prior separation of the matrix elements from a suitable aliquot (100 ml) of the solution by the basic lead carbonate procedure (p 21).

13. For the most accurate determination of the sodium and potassium contents of the reagent blank solution, the largest possible aliquot of the solution (or the initial solution after the addition of 10 ml of radiation buffer solution and dilution to volume) should be employed for subsequent measurement.

14. If the sample contains moderate amounts of lithium (i.e., greater than the sodium or potassium content) or rubidium and/or cesium, equivalent amounts of these elements must be added to the standard calibration solutions.

15. If the sample is a wulfenite ore or mill product, any lead sulphate that is present at this stage can be removed by filtering the solution into the separatory funnel.

16. Approximately 2-2.5 ml of 9% cupferron solution are usually sufficient for the complexation of 10 mg of metal ion. To test for completeness of precipitation, extract the solution twice with chloroform, then add 1-2 ml of cupferron solution. Complete precipitation is indicated by a transient white precipitate resulting from the presence of excess cupferron.

17. The cupferron-chloroform extraction procedure can also be used for the separation of large amounts of iron from solutions of iron ores and mill products. However, Procedure B is recommended for the analysis of these materials because the mercury cathode separation procedure yields a considerably lower reagent blank than the cupferron-chloroform extraction procedure.

18. The decomposition of a small amount of sample is recommended because filtration of large amounts of the hydrous oxides of niobium and tantalum is slow.

19. Repeated treatment of the sample with hydrochloric, nitric, and hydrofluoric acids may be required to obtain complete decomposition.

20. If the sample solution has been inadvertently evaporated to dryness, add 1-2 ml of concentrated hydrofluoric acid and 6-7 ml of 50% sulphuric acid. Evaporate the solution to fumes of sulphur trioxide 3 or 4 times to ensure the complete removal of hydrofluoric acid, then proceed as described.

21. Peptization of the hydrous oxides occurs if the solution is allowed to cool appreciably during filtration, or if the precipitate is washed with cold water.

22. If the initial precipitation of niobium and tantalum was incomplete, and more hydrolysis occurs during evaporation of the filtrate, re-filter the solution, then proceed as described.

Calculations

$\%Na_2O = 1.348 \times \%\ Na$

$\%K_2O = 1.205 \times \%\ K$

Other applications

The method described in Procedure A can be employed to determine sodium and potassium in ceramic materials (e.g., flint clay, and firebrick), glass, asbestos, cryolite, and coal and wood ash. The method described in Procedure D is applicable to alkali fluo- and chloro-titanates[1].

References

1. Elsie M. Penner (Donaldson) and W.R. Inman, "Flame Photometric Methods Used in the Mineral Sciences Division", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB24, September (1961).

2. W.T. Elwell and J.A.F. Gidley, "Atomic-Absorption Spectrophotometry", The MacMillan Company, New York, pp 25-36 (1962).

3. H.V. Malmstadt and W.E. Chambers, Anal. Chem., 32, 225 (1960).

4. C.A. Baker and F.W.J. Garton, U.K. At. Energy Authority, Res. Group Rept., AERE R-3490 (1961).

5. H. Sanui and N. Pace, Appl. Spectry., 20, 135 (1966).

DETERMINATION OF POTASSIUM AND SODIUM IN REFRACTORY AND ACID-SOLUBLE SILICATE ROCKS AND MINERALS, CARBONATE ROCKS, CLAY, SHALE, PHOSPHATE ROCK, KYANITE, AND BAUXITE BY A MODIFIED J. LAWRENCE SMITH METHOD

Principle

This method[1] is a modification of that developed by Biffen[2], and involves sample decomposition by the J. Lawrence Smith Method. Potassium and sodium are determined, either by atomic-absorption spectrophotometry or by emission flame-photometry, at 589.0 and 766.5 nm, respectively, in a slightly oxidizing air-acetylene flame, after the extraction of their chlorides from the resultant sinter with water.

Outline

The sample is heated with a dry mixture of calcium carbonate and ammonium chloride to convert sodium and potassium to soluble chlorides. The sintered mass is digested with hot water, and the resultant calcium oxide, and various matrix elements (silicon, aluminum, iron, magnesium, beryllium, titanium, manganese, barium, and phosphate) that are retained in the precipitate in the form of insoluble oxides and complex silicates and aluminates, are removed by filtration. The resulting filtrate is ultimately analyzed for sodium and potassium.

Discussion of interferences

Lithium, rubidium, cesium, and calcium are not separated from sodium and potassium by filtration of the aqueous solution obtained after sample decomposition by the J. Lawrence Smith method and digestion of the resulting sinter in water[3]. These elements interfere in the determination of sodium and potassium, both by atomic-absorption spectrophotometry and by emission-flame photometry, by enhancing their absorption and emission[1,4-6]. Interference from calcium, and error resulting from the presence of small amounts of alkali metals in the calcium carbonate and ammonium chloride employed for sample decomposition, is compensated for by adding identical aliquots of a reagent blank solution to the standard sodium and potassium calibration solutions[1]. Ionization interference from lithium, rubidium, and cesium, and mutual ionization interference from potassium in the determination of sodium and vice versa, is compensated for by adding the approximate amounts of these elements, present in the final sample solution, to the standard calibration solutions[1].

Range

The method is suitable for samples containing more than approximately 0.01% of sodium and/or potassium.

Reagents

Standard sodium, potassium, and combined sodium and potassium solutions, 100 ppm. Prepare as described in the Radiation Buffer Method for potassium and sodium (p 27).

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Preparation of standard calibration solutions

Transfer 5 g of calcium carbonate (low alkali metal content) and 0.5 g of ammonium chloride to an approximately 6 by 6-inch piece of glazed paper, mix thoroughly with a spatula, then, using a brush, transfer the mixture to a 30-ml platinum crucible (Note 1). Cover, and place the crucible in a hole, punched in a 6 by 6-inch piece of heavy asbestos sheet, so that at least one-third of its height is above the top of the sheet (Note 2). Heat the mixture at a low temperature with a bunsen burner for approximately 15 minutes, or until the odor of ammonia is no longer perceptible (Note 3), then gradually raise the temperature to the full heat of the burner, and maintain the mixture at this temperature for 45 minutes. Cool, remove the cover, wash the outside of the crucible with water

(Note 4), and transfer the crucible and contents to a 600-ml Teflon or stainless steel beaker (Note 5). Add sufficient water to cover the crucible, and cover the beaker with a Teflon or steel cover. Heat the solution gently for approximately 1 hour, then remove the crucible after washing it thoroughly with water.

Evaporate the solution to approximately 150 ml, filter the hot solution (Whatman No. 40 paper) into a 250-ml volumetric flask and, using a thick glass rod, break up any lumps remaining in the beaker. Using a jet of hot water, wash the precipitate remaining in the beaker into the filter paper, and wash the paper and precipitate thoroughly with hot water. Discard the precipitate. Add 1 drop of 0.1% methyl red solution to the filtrate, and neutralize it by the addition of concentrated hydrochloric acid, by drops, until the solution is just pink. Cool the resulting solution to room temperature, dilute to volume with water and mix (Note 6).

Depending on the expected sodium and potassium contents of the sample solution, add aliquots (5-50 ml) of the above reagent blank solution, identical to the aliquot of the sample solution (prepared as described below) taken for the determination of the desired element, to an appropriate number of 100-ml volumetric flasks. By burette, add suitable increments of the dilute standard 100-ppm sodium and potassium solutions or the combined solution (Note 7). Dilute each solution to volume with water and mix (Note 8).

Procedure

Depending on the expected sodium and potassium contents, decompose and treat 0.25-0.5 g of powdered sample (Note 9), ground to at least minus 200 mesh (Note 10), by the method described above for the preparation of the reagent blank solution (Notes 11 and 12).

Transfer 5-50-ml aliquots of the resulting solution (Note 13) to 100-ml volumetric flasks, dilute to volume with water and mix. Measure the sodium and potassium absorbances or emissions of the diluted solutions, at 589.0 and 766.5 nm, respectively, in a slightly oxidizing air-acetylene flame. Determine the sodium and potassium contents of the aliquots by relating the resulting values to those obtained concurrently for standard sodium and potassium solutions of slightly higher and lower concentrations (Notes 7 and 14).

Notes

1. *If one or more samples, particularly those with low sodium and/or potassium contents, are to be analyzed, two or more of the subsequent reagent blank solutions should be prepared (Note 7). If desired, the resulting solutions may be combined, either after filtration and dilution to volume, or by filtration into a volumetric flask of appropriate size.*

2. The upper part of the crucible provides a relatively cool area for the condensation of any alkali metal chlorides that may volatilize during the heating stage[7].

3. During the initial heating stage, calcium chloride, ammonia, water, and carbon dioxide are formed, according to the following reaction:

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + CO_2 + H_2O.$$

If the initial temperature is too high, direct volatilization of ammonium chloride, indicated by dense white fumes, will occur[7].

4. To avoid contamination of the subsequent reagent blank solution with sodium from the hands, the platinum crucible should be handled with clean tongs at this stage.

5. Glass beakers should not be employed. The corrosive action of the subsequent alkaline solution on the glass will result in the contamination of the solution by alkali metals, particularly sodium, from the glass.

6. If a delay of more than 1 day is necessary before the preparation of the subsequent standard calibration solutions, transfer the reagent blank solution to a polyethylene bottle to avoid contamination of the solution by alkali metals from the glass.

7. Because sodium interferes in the determination of potassium and vice versa, both by atomic-absorption spectrophotometry and, particularly, by emission flame-photometry, especially in high-temperature flames, standard calibration solutions containing equal amounts of sodium and potassium should be employed only for the analysis of samples that also contain approximately equal amounts (±5 ppm) of both elements. For accurate analysis, a prior estimate of the sodium and potassium contents of the final, diluted sample solution should be made, using appropriate standard solutions containing identical aliquots of the reagent blank solution and equal amounts of sodium and potassium. Subsequently, suitable standard solutions, in which the equivalent amount of potassium present in the diluted sample solution is added to the standard sodium solutions and vice versa, should be prepared (using the dilute standard sodium and potassium solutions) and employed for the analysis of the sample solution.

8. The resulting calibration solutions can be kept for approximately 1 month, if stored in polyethylene bottles (Note 6). However, these solutions can be employed for subsequent analyses only if the same batches of calcium carbonate and ammonium chloride are used for sample decomposition.

9. This procedure is applicable to almost all refractory silicate materials (e.g., tourmaline, cordierite, pyrophyllite muscovite, and garnet), and to all the acid-soluble silicate materials listed in Note 6 of the Radiation Buffer Method for potassium and sodium (p 30), including clay and shale, and samples with high phosphorus contents. It is not applicable to niobium and tantalum minerals, ores, or slags[1].

10. Because sample decomposition involves a sintering, rather than a fusion process, the sample must be finely-ground and thoroughly mixed with the calcium carbonate and ammonium chloride to obtain complete decomposition.

11. The completeness of sample decomposition can be tested by dissolving the precipitate in dilute hydrochloric acid, and visually examining the resulting solution for undecomposed material.

12. If the sample solution cannot be analyzed for sodium and potassium on the same day that it is prepared, transfer it to a polyethylene bottle (Note 6).

13. The resulting sample solution cannot be used for the determination of lithium because some lithium is retained in the precipitate during filtration[3].

14. If the sample contains moderate amounts of lithium (i.e., greater than the sodium or potassium content) or rubidium and/or cesium, equivalent amounts of these elements must be added to the standard calibration solutions.

Calculations

$\%Na_2O = 1.348 \times \%\ Na$

$\%K_2O = 1.205 \times \%\ K$

Other applications

This method can be employed to determine sodium and potassium in ceramic materials (e.g., flint clay, and firebrick), glass, cement, aluminum oxide, asbestos, and coal and wood ash[1].

References

1. Elsie M. Penner (Donaldson) and W.R. Inman, "Flame Photometric Methods Used in the Mineral Sciences Division", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB24, September (1961).

2. F.M. Biffen, Anal. Chem., 22, 1014 (1950).

3. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 75-77, 184-185 (1938).

4. H.V. Malmstadt and W.E. Chambers, Anal. Chem., 32, 225 (1960).

5. C.A. Baker and F.W.J. Garton, U.K. At. Energy Authority, Res. Group Rept., AERE R-3490 (1961).

6. H. Sanui and N. Pace, Appl. Spectry., 20, 135 (1966).

7. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 925-929 (1953).

DETERMINATION OF SILVER IN SILVER, LEAD, ZINC AND COPPER ORES AND MILL PRODUCTS

Principle

This method[1] is a modification of that developed by Greaves[2], and is based on the formation of a stable soluble silver compound by complexation with diethylenetriamine. Silver is determined, in an approximately 0.6 M hydrochloric acid solution of the sample, by atomic-absorption spectrophotometry, at 328.1 nm, in an oxidizing air-acetylene flame.

Outline

The sample is leached with hydrochloric, nitric, and perchloric acids, and the solution is evaporated to near dryness to remove excess acids. Soluble and insoluble silver and lead compounds are ultimately complexed and dissolved, respectively, with diethylenetriamine. The resultant hydrous oxide precipitate is re-dissolved with hydrochloric acid, and insoluble material is removed by filtration. The resulting filtrate is analyzed for silver.

Discussion of interferences

Moderate amounts of anions and cations, including platinum, palladium, rhodium, and gold, do not interfere in the determination of silver in an air-acetylene flame[3-5]. Prior complexation of silver and lead with diethylenetriamine eliminates interference and error resulting from the precipitation of these elements as insoluble chlorides before or during atomization of the sample solution. This technique also reduces burner corrosion because it eliminates the necessity for the strong hydrochloric acid medium (approximately 3 M) normally required to maintain silver in solution, prior to its determination by atomic-absorption spectrophotometry[1,2].

Range

The method is suitable for samples containing approximately 0.1 to 600 oz/ton or 0.0003 to 2% of silver, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard silver solution, 100 ppm. Dissolve 0.1000 g of pure silver foil by heating gently with 40 ml of 25% nitric acid. Cool, and dilute to 1 litre with 10% nitric acid.

Nitric acid, 25% and 10% v/v.

Hydrochloric acid, 25% and 5% v/v.

Diethylenetriamine. Technical-grade.

Preparation of standard calibration solutions

To an appropriate number of 100-ml volumetric flasks, add, by burette, suitable varying increments of the standard 100-ppm silver solution. Dilute each solution to volume with 10% nitric acid and mix.

Procedure

Depending on the expected silver content, transfer 0.5 g -0.1 assay-ton (Notes 1 and 2) of powdered sample, ground to at least minus 200 mesh (Note 3), to a 400-ml beaker. Add 25 ml of concentrated hydrochloric acid, cover the beaker, and gently heat the mixture below the boiling point for approximately 20 minutes (Note 4). Cautiously add 15 ml of concentrated nitric acid, in small portions, and allow the mixture to digest on a hotplate for about 30 minutes. Cool, add 10 ml of concentrated perchloric acid, partly uncover the beaker and, without baking, evaporate the solution to near dryness. Cool, wash down the sides of the beaker and the cover with approximately 25 ml of 25% hydrochloric acid, and boil the solution for 10-15 minutes to ensure the complete dissolution of the soluble salts.

Cool the solution to room temperature and, while stirring, cautiously add sufficient diethylenetriamine to produce a permanent hydrous oxide precipitate (Note 5). Add sufficient concentrated hydrochloric acid, in small portions, to dissolve the precipitate, then add 10 ml in excess. Filter the resulting solution (Whatman No. 40 paper) into a 200-ml volumetric flask, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue. Cool the filtrate to room temperature, dilute to volume with water and mix.

Measure the absorbance of the resulting solution, or a suitable aliquot diluted to an appropriate volume with 5% hydrochloric acid, at 328.1 nm, in an oxidizing air-acetylene flame. Determine the silver content of the solution or aliquot by relating the resulting value to those obtained concurrently for standard silver solutions of slightly higher and lower concentrations.

Notes

1. One-tenth of an assay-ton = 2.9166 g of sample.

2. If the sample is a lead sulphide concentrate, 1 g or less should be taken[2]. Lead, in large amounts, may not be completely complexed during the subsequent treatment of the sample solution with diethylenetriamine, and may interfere with, or prevent complete complexation of the silver.

3. Complete extraction or leaching of silver from its matrix material may not be obtained if the sample is in a coarser state.

4. Treatment of the sample with hydrochloric acid, prior to the addition of nitric acid as oxidant, removes the bulk of the sulphide sulphur as hydrogen sulphide.

5. Elements that precipitate as hydrous oxides under these conditions are, in general, those that form precipitates in dilute ammoniacal media.

Calculations

$$\text{Ag (troy oz/ton)} = \frac{\text{Silver found (mg)}}{\text{Sample weight (mg)}} \times 29166.$$

References

1. P.E. Moloughney, "Assay Investigation for Silver Content on Mine Standards", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Test Report AC 71-48, September (1971).

2. M.C. Greaves, Nature, 199, 552 (1963).

3. W. Slavin, "Atomic Absorption Spectroscopy", Interscience, New York, pp 158-160, 247-248 (1968).

4. B.S. Rawling, M.D. Amos and M.C. Greaves, Australasian Inst. Mining and Met. Proc., 199 (1961).

5. P.E. Moloughney and J.A. Graham, Talanta, 18, 475 (1971).

PART II

LIGHT-ABSORPTION SPECTROPHOTOMETRIC METHODS

DETERMINATION OF ARSENIC IN ORES AND MILL PRODUCTS BY THE MOLYBDENUM BLUE METHOD AFTER DISTILLATION AS ARSENIC TRICHLORIDE

Principle

This method[1] is based on that developed by Rodden[2], and involves the formation of the reduced heteropoly arsenomolybdic acid complex in a 0.23 M sulphuric acid-0.001 M ammonium molybdate medium in the presence of hydrazine sulphate as reductant. Arsenic is determined by spectrophotometric measurement, at approximately 845 nm, of the absorbance of the blue reduced complex.

Outline

Following the separation of arsenic from matrix elements by distillation as the trichloride as described in the Volumetric-Distillation-Bromate Method for arsenic (Procedures A and B, pp 236 and 237, Note 14), the distillate is ultimately analyzed for arsenic, after oxidation of arsenic (III) to the pentavalent state with nitric acid.

Discussion of interferences

Germanium, if present in moderate amounts, and phosphorus as orthophosphate, interfere in the determination of arsenic because they form similar reduced heteropoly molybdic acid complexes under the conditions employed for the formation of the arsenic complex. Vanadium, tungsten, niobium, tantalum, lead, barium, strontium, zirconium, mercury, silver, antimony, bismuth, cadmium, chromium, copper, iron, zinc, gold, selenium, tellurium, and titanium also interfere if they are present in large amounts[3-8]. Silicon forms a heteropoly complex with ammonium molybdate in dilute acid media, but moderate amounts do not interfere in the determination of arsenic because the yellow complex is not reduced to the blue silicomolybdic acid complex under the conditions (i.e., acidity) employed for the formation and reduction of the arsenomolybdic acid complex[3,6,8].

With the exception of germanium and selenium, interference from all of the above elements, and from coloured ions (nickel, cobalt, copper, chromium, cerium, and uranium) is avoided by separating arsenic from these elements, and from various other elements (aluminum, beryllium, calcium, indium, gallium, magnesium, manganese, rhenium, thallium, thorium, tin, the platinum metals, and the rare earth elements) by distillation as the trichloride from an approximately 8 M hydrochloric acid medium[1-3,5,8]. Germanium is quantitatively volatilized as the tetrachloride under the conditions employed for the distillation of arsenic[3,8], and antimony is partly co-distilled as the trichloride at temperatures (i.e., vapour temperature) greater than 107°C[8,9], and at 105°C if the amount of antimony present during distillation greatly exceeds that of arsenic[9]. Microgram-quantities of germanium[3,6] and milligram-quantities of antimony[2,3,8] do not cause significant error in the arsenic result.

Oxalic, tartaric, and citric acids, and fluoride, bromide, and oxidizing agents interfere in this method[4]. Reducing agents, other than hydrazine sulphate, should not be present during complex formation.

Range

The method is suitable for samples containing approximately 0.0002 to 3.5% of arsenic.

Reagents

Standard arsenic solution (1 ml = 0.1 mg of arsenic). Dissolve 0.1320 g of pure arsenic trioxide (As_2O_3) in 100 ml of concentrated hydrochloric acid (Note 1), add approximately 200 ml of water, cool, and dilute to 1 litre with water. Dilute 50 ml of this stock solution to 500 ml with water (1 ml = 10 µg of arsenic).

Ammonium molybdate solution, 1% w/v. Dissolve 5 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in approximately 300 ml of 2.3 M sulphuric acid and dilute to 500 ml with the same solution. Store in a polyethylene bottle.

Hydrazine sulphate solution, 0.5% w/v. Prepare a fresh solution daily.

Ammonium molybdate-hydrazine sulphate solution, 0.1% and 0.005% w/v, respectively. Dilute 100 ml of 1% ammonium molybdate solution to approximately 900 ml with water, add 10 ml of 0.5% hydrazine sulphate solution, dilute to 1 litre with water and mix. Prepare fresh as required (Note 2).

Sulphuric acid, 2.3 M. Add 128 ml of concentrated sulphuric acid, slowly and while stirring, to approximately 850 ml of water in a 1500-ml pyrex beaker. Allow the solution to cool to room temperature, transfer to a 1-litre volumetric flask, and dilute to volume with water.

Calibration curve

To six 150-ml beakers (Note 3), add, by burette, 0.5, 1, 2, 5, 10, and 15 ml, respectively, of the dilute standard 10 µg/ml arsenic solution, and dilute each solution to approximately 15 ml with water. Add 15 ml of water to a seventh beaker; this constitutes the blank. Add 15 ml of concentrated nitric acid to each beaker, evaporate the solution to dryness in a water-bath, and bake the residue in an oven for 30-60 minutes at approximately 130°C (Note 4) to ensure the complete removal of nitric acid. Cool, add 30 ml of 0.1% ammonium molybdate-0.005% hydrazine sulphate solution, and warm gently to dissolve the residue. Transfer the solution to a 50-ml volumetric flask, using the ammonium molybdate-hydrazine sulphate solution to wash the beaker, and dilute to approximately 45 ml with the same solution. Heat the flask in a boiling water-bath for 15 minutes, cool to room temperature, dilute to volume with the ammonium molybdate-hydrazine sulphate solution and mix (Note 5). Determine the absorbance of each reduced arsenomolybdic acid solution, at 845 ± 5 nm (Note 6), against the blank as the reference solution, using 1-cm cells. Plot µg of arsenic vs. absorbance.

Procedure

Following the separation of arsenic by distillation as the trichloride as described in Procedures A and B (pp 236 and 237, Note 14) of the Volumetric-Distillation-Bromate Method for arsenic, transfer the distillate to a 250-ml volumetric flask (Note 7), dilute to volume with water and mix.

Transfer a 5-50-ml aliquot of both the sample and blank solutions, depending on the expected arsenic content, to 150-ml beakers, add 15 ml of concentrated nitric acid, and evaporate the solutions to approximately 15-20 ml on a hot-plate. Place the beakers in a water-bath, and evaporate the solutions to dryness. Bake the residue in an oven for 30-60 minutes to ensure the complete removal of nitric acid, and proceed with the formation of the blue reduced arsenomolybdic acid complex as described above. Measure the absorbance of the sample solution against the reagent blank solution, and determine the arsenic content of the aliquot by reference to the calibration curve.

Notes

1. If necessary, the hydrochloric acid solution may be warmed gently to aid the decomposition of the arsenic trioxide, but it should not be allowed to boil or else arsenic trichloride may be lost by volatilization.

2. The mixed ammonium molybdate-hydrazine sulphate solution is unstable and should be prepared just before it is required. A solution that has stood for more than 1 hour should not be employed[1,7].

3. Glassware should be previously soaked in 25% ammonium hydroxide, and then cleaned with concentrated nitric acid and washed with water to avoid contamination from phosphate-bearing soaps or detergents.

4. If the residue is baked at temperatures exceeding approximately 140°C, arsenic may be lost, presumably by volatilization, as the pentachloride[2,5,8].

5. The blue reduced arsenomolybdic acid complex that is formed under these conditions is stable for at least 2 hours[1].

6. The reduced arsenomolybdic acid complex exhibits an intense absorption band in the wavelength range from approximately 830 to 860 nm[7]. The exact wavelength of maximum absorption of the complex should be determined by measuring the absorbance of one of the reduced arsenomolybdic acid solutions (e.g., the 100 µg arsenic solution) in the above wavelength range, at 5 nm intervals, against the blank.

7. If a double distillation of arsenic trichloride was performed to separate small amounts of co-distilled antimony trichloride from the initial distillate, prior to the determination of antimony in the solution remaining in the distillation flask by the Volumetric-Bromate Method (p 230, Note 12), transfer the distillate to a 500-ml volumetric flask, dilute to volume with water, and proceed as described. If the sample contains considerably more antimony than arsenic, and antimony is not to be determined in the solution remaining in the distillation flask, the separation of co-distilled antimony by double distillation is not necessary. Small amounts of antimony do not interfere in the determination of arsenic by the reduced arsenomolybdic acid method[2,3,8].

Calculations

$\%As_2O_3 = 1.320 \times \%\ As$

$\%As_2O_5 = 1.534 \times \%\ As$

Other applications

This method can be employed to determine arsenic in lead- and tin-base solder metals, and in various metals and alloys if the sample is decomposed by treatment with potassium pyrosulphate and sulphuric acid[10,11]. It is also applicable to silicate rocks and minerals, following sample decomposition by fusion with sodium carbonate and potassium nitrate, or with sodium carbonate and sodium peroxide[8]. With modifications in the decomposition procedure, it is also applicable to ferrosilicon and silicon metal[1], and to iron, steel, brass, bronze, pig lead, and tin[2,8].

References

1. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E360, pp 932-933 (1971).

2. C.J. Rodden, J. Res. Natl. Bur. Std., <u>24</u>, 7 (1940).

3. A.L. Chaney and H.J. Magnuson, Ind. Eng. Chem., Anal. Ed., <u>12</u>, 691 (1940).

4. J.T. Woods and M.G. Mellon, ibid., <u>13</u>, 760 (1941).

5. J.A. Sultzaberger, ibid., <u>15</u>, 408 (1943).

6. C.L. Luke and M.E. Campbell, Anal. Chem., <u>25</u>, 1588 (1953).

7. D.F. Boltz and M.G. Mellon, ibid., <u>19</u>, 873 (1947).

8. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 278-279, 282-288, 291-292, 294-295 (1959).

9. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 70-73 (1953).

10. N.H. Furman, "Scott's Standard Methods of Chemical Analysis". 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 128-130 (1962).

11. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, pp 263-264, 380-381 (1971).

DETERMINATION OF BISMUTH IN ORES AND MILL PRODUCTS BY THE IODIDE METHOD

Principle

Bismuth is determined by spectrophotometric measurement, at 460 nm, of the absorbance of the yellow iodobismuthite ion, formed in a 0.5 M sulphuric acid - 0.12 M potassium iodide medium, in a reducing (hypophosphorous acid) environment[1,2].

Outline

The sample is decomposed with nitric acid, and acid-insoluble material is removed by filtration. The resulting filtrate is analyzed for bismuth.

Discussion of interferences

Hypophosphorous acid, which is produced by the reaction of a mineral acid with sodium hypophosphite, eliminates interference from free iodine during complex formation. This reductant prevents the air-oxidation of iodide ion to iodine, and destroys any iodine formed by the reaction of iodide ion with various oxidizing ions [e.g., iron (III), and copper (II)] that may be present in the sample solution[1,2].

Coloured ions (nickel, cobalt, chromium, and uranium), and ions that form coloured compounds with iodide (platinum, palladium, antimony, and tin) interfere in this method[1]. Lead, which precipitates as the sulphate, and copper and silver, which precipitate as iodides during complex formation, interfere, if present in large amounts, because the precipitates occlude bismuth[1,2]. Small amounts of these elements do not cause appreciable error in the bismuth result if the precipitates are removed by centrifugation or filtration. Moderate amounts of molybdenum, titanium, and zirconium do not interfere.

Range

The method is suitable for samples containing approximately 0.03 to 10% of bismuth, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard bismuth solution (1 ml = 2 mg of bismuth). Dissolve 0.5000 g of pure bismuth metal by heating with 30 ml of 30% nitric acid. Boil the resulting solution gently for approximately 10 minutes to expel oxides of nitrogen, then cool, and dilute to 250 ml with water. Dilute 10 ml of this stock solution to 200 ml with water (1 ml = 0.1 mg of bismuth).

Potassium iodide solution, 10% w/v.

Sodium hypophosphite solution, 30% w/v.

Sulphuric acid, 50% v/v.

Calibration curve

To six 50-ml volumetric flasks, add, by burette, 1, 2, 4, 6, 8, and 10 ml, respectively, of the dilute standard 0.1 mg/ml bismuth solution, and dilute each solution to approximately 15 ml with water. Add 15 ml of water to a seventh flask; this constitutes the blank. Add 3 ml of 50% sulphuric acid, 1 ml of 30% sodium hypophosphite solution, and 10 ml of 10% potassium iodide solution to each flask, in succession, mix thoroughly, and allow the solutions to stand for 10 minutes (Note 1). Dilute to volume with water, mix, and determine the absorbance of each solution, at 460 nm, against water as the reference solution, using 1-cm cells. Correct the absorbance value obtained for each bismuth-iodide solution by subtracting that obtained for the blank solution. Plot mg of bismuth vs. absorbance.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.25-1 g of powdered sample, depending on the expected bismuth content, to a 250-ml beaker, moisten with water, and add 15 ml of concentrated nitric acid. Cover, and boil gently (Note 2) until the decomposition of the sample or the acid-soluble material is complete (Note 3), then add 50 ml of water, and boil the solution to expel oxides of nitrogen. Filter the resulting solution (Whatman No. 40 paper) into a volumetric flask of appropriate size (100-250 ml), and wash the beaker, paper, and residue thoroughly with hot water (Note 4). Discard the paper and residue. Cool the filtrate to room temperature, dilute to volume with water and mix.

Transfer a 5-10-ml aliquot of both the sample and blank solutions to 50-ml volumetric flasks, and proceed with the formation of the bismuth-iodide complex, and the subsequent measurement of the absorbance as described above (Note 5). Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution, and determine the bismuth content of the aliquot by reference to the calibration curve.

Notes

1. Because reduction with hypophosphorous acid is slow, a standing period of 10 minutes is recommended to ensure the complete destruction of any free iodine that is formed by the reaction of iodide ion with oxidizing sample constituents.

2. Do not allow the sample solution to evaporate to dryness at this stage. If large amounts of silica are present, dehydration may result in loss of bismuth because of the formation of an insoluble oxy compound that is occluded by silica[3].

3. Some insoluble residue (e.g., silicates, metastannic acid, hydrated tungsten trioxide, titanium and zirconium compounds) may be present at this stage.

4. If yellow hydrated tungsten trioxide is present, 2% nitric acid should be employed as a wash solution to prevent peptization of the precipitate.

5. Suspended matter, causing turbidity in the final solution, may be removed by centrifuging or filtering the solution before measuring the absorbance of the bismuth-iodide complex.

References

1. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 331-336 (1959).

2. D.T. Englis and B.B. Burnett, Anal. Chim. Acta, 13, 574 (1955).

3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 232 (1953).

DETERMINATION OF CHROMIUM IN IRON ORES AND MILL PRODUCTS, AND SILICATE ROCKS AND MINERALS BY THE s-DIPHENYLCARBAZIDE METHOD

Principle

Chromium is determined by spectrophotometric measurement, at 540 nm, of the absorbance of the red-violet 2:3 complex formed between chromium (VI) and s-diphenylcarbazide in a 0.1 M sulphuric acid medium, after oxidation of chromium to the hexavalent state in a 0.25 M sulphuric acid medium with ammonium persulphate in the presence of silver nitrate as catalyst[1-3].

Outline

Iron ores and mill products, and silicate rocks and minerals are decomposed by fusion with sodium peroxide, and with a mixture of sodium carbonate and sodium peroxide, respectively, to convert chromium to soluble chromate ion. The melt is digested in water, and the hydrous oxides of certain interfering elements [manganese, iron (III), copper (II), cobalt, and nickel], and various other elements (titanium, zirconium, magnesium, and calcium) are removed by filtration. Vanadium, if present in large amounts, is separated from chromium by chloroform extraction of its 8-hydroxyquinoline complex. The resulting solution, or the preceding solution, if large amounts of vanadium are absent, is ultimately analyzed for chromium.

Discussion of interferences

Copper (II), cobalt, and nickel interfere in the determination of chromium because of the background colours imparted to the solution. Manganese interferes because of the simultaneous formation of the purple permanganate ion during the oxidation procedure. Iron (III) interferes because of the formation of a brown or yellow-brown complex with diphenylcarbazide[1].

Prior to the formation of the chromium complex, all of the above interfering elements are separated from chromium by filtration of their hydrous oxides, after digestion of the sodium peroxide or the mixed sodium carbonate and sodium peroxide melt in water. Vanadium (V) is not separated from chromium by this procedure and interferes by forming a strongly coloured yellow complex with diphenylcarbazide[2]. Because of the instability (i.e., colour fading) of this complex, interference from small amounts of vanadium (less than 10 times the amount of chromium present) is readily eliminated or minimized by allowing the sample solution to stand for approximately 10 minutes before measuring the absorbance of the chromium complex[1]. Interference from large amounts of vanadium is avoided by separating it from chromium by chloroform extraction of its 8- hydroxyquinoline complex from a slightly acid (approximately pH 4) medium[1,2].

Molybdenum (VI), mercury (I) and mercury (II) form violet and violet-blue complexes, respectively, with diphenylcarbazide, but because of the low sensitivity of these complexes, up to approximately 20 mg of these elements do not interfere[2]. Oxidizing and reducing agents interfere during complex formation. Barium and lead cause low results for chromium because they form insoluble chromates which are removed with the hydrous oxide precipitate during the initial filtration of the sample solution[3].

Range

The method is suitable for iron ores and mill products containing approximately 0.002 to 1% of chromium, and for silicate rocks and minerals containing more than approximately 0.001% of chromium.

Reagents

Standard chromium solution (1 ml = 0.1 mg of chromium). Dissolve 0.2829 g of pure potassium dichromate (dried at 105°C for 1-2 hours) in water and dilute to 1 litre. Dilute 25 ml of this stock solution to 250 ml with water (1 ml = 10 μg of chromium) (Note 1).

s-Diphenylcarbazide (1,5-diphenylcarbohydrazide) solution, 0.25% w/v in water-free acetone (Note 2).

Silver nitrate solution, 1% w/v.

Ammonium persulphate solution, 10% w/v. Prepare fresh as required.

8-Hydroxyquinoline (8-quinolinol) solution, 0.25% w/v. Dissolve 0.125 g of the reagent in 0.5 ml of concentrated acetic acid, and dilute to 50 ml with water.

Sulphuric acid, 2 M. Add 55 ml of concentrated sulphuric acid, slowly and while stirring, to approximately 400 ml of water in a 1-litre pyrex beaker. Cool to room temperature, transfer to a 500-ml volumetric flask, and dilute to volume with water.

Ammonium hydroxide, 10% v/v.

Sodium carbonate wash solution, 1% w/v.

Chloroform, Analytical reagent-grade.

Double-distilled water, or distilled water free of reducing substances.

Calibration curves

Add 5 ml of 2 M sulphuric acid to each of eight 150-ml beakers; then, by burette, add to the last seven beakers, 0.5, 1, 2, 3, 5, 8, and 10 ml, respectively, of the dilute standard 10 µg/ml chromium solution. The contents of the first beaker constitute the blank. Dilute the contents of each beaker to approximately 40 ml with water, add 1 ml of 1% silver nitrate solution and 5 ml of 10% ammonium persulphate solution, cover the beakers, and boil the solutions for 10-20 minutes to ensure the complete decomposition of the excess persulphate (Note 3). Cool to room temperature and, if necessary, filter the resulting solutions (Whatman No. 40 paper) into 100-ml volumetric flasks to remove any precipitated silver chloride. Dilute each solution to approximately 90 ml with double-distilled water, or distilled water free of reducing substances, and add 2 ml of 0.25% diphenylcarbazide solution (Notes 4 and 5). Dilute to volume with water, mix, and allow the solutions to stand for 10 minutes. Determine the absorbance of each of the first four chromium-diphenylcarbazide solutions, at 540 nm, against the blank as the reference solution, using 5-cm cells. Determine the absorbance of each of the last five solutions in a similar manner, using 1-cm cells. Plot µg of chromium vs. absorbance for each series of measurements.

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Iron ores and mill products

(a) Vanadium:chromium ratio less than 10:1

Transfer 0.4-1 g of powdered sample, depending on the expected chromium content, to a 30-ml porcelain, nickel, or chromium-free iron crucible (Note 6), add a ten-fold weight excess of sodium peroxide and mix thoroughly. Cover the crucible, fuse the mixture over a low flame, and maintain it in the molten state for several minutes to ensure complete sample decomposition. Allow the melt to cool, then transfer the crucible and cover to a 400-ml (covered) beaker containing approximately 100 ml of water. When the subsequent reaction has ceased, remove the crucible and cover after washing them thoroughly with hot water, and boil the solution for at least 10 minutes to destroy the residual peroxide (Note 7). Filter the resulting solution (Whatman No. 540 paper) into a 200-ml volumetric flask, and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the paper and precipitate. Cool the filtrate to room temperature, dilute to volume with water and mix.

Transfer a 5-25-ml aliquot of both the sample and blank solutions to 150-ml beakers, and, if necessary, dilute to 20-25 ml with water. Using a pH meter, neutralize the solutions to pH 7 ± 0.5 (Note 8) with 2 M sulphuric acid and/or more dilute sulphuric acid as required. Add 5 ml of 2 M sulphuric acid, dilute the resulting solutions to approximately 40 ml with water, and proceed with the silver nitrate-ammonium persulphate oxidation of chromium (Note 9), and the subsequent formation of the diphenycarbazide complex as described above (Note 5).

Allow the solutions to stand for 10 minutes, then measure the absorbance of the sample solution against the reagent blank solution, using either 1- or 5-cm cells as required, and determine the chromium content of the aliquot by reference to the appropriate calibration curve.

(b) Vanadium:chromium ratio more than 10:1

Transfer a 5-25-ml aliquot of both the sample and blank solutions, obtained after filtration of the aqueous solution of the sodium peroxide melt, to 50-ml beakers. If necessary, dilute the solutions to approximately 25 ml with water and, using a pH meter, adjust the pH to approximately 4 with 2 M sulphuric acid (Note 10). Transfer the solutions to 60-ml separatory funnels, add 1 ml of 0.25% 8-hydroxyquinoline solution (Note 11), mix, and extract the resulting reddish-black vanadium-8-hydroxyquinoline complex, by shaking for 30-60 seconds each time, with two 5-ml portions of chloroform. Discard each extract. Add an additional 1-ml portion of 8-hydroxyquinoline solution, and re-extract the solutions 2 or 3 more times, as described above, until the chloroform phase is essentially colourless. Transfer the solutions to 150-ml beakers, warm gently to remove the residual chloroform, then evaporate the solutions to 20-25 ml. Cool, neutralize the solutions to pH 7 ± 0.5 (Note 8) with 10% ammonium hydroxide and/or more dilute ammonium hydroxide as required. Add 5 ml of 2M sulphuric acid, dilute the resulting solutions to approximately 40 ml with water, and proceed with the oxidation and subsequent determination of chromium as described above.

B - Silicate rocks and minerals

Transfer 1-2 g of powdered sample, depending on the expected chromium content, to a 30-ml platinum crucible, and ignite at approximately 400°C for about 10 minutes (Note 12). Cool, add 5 g of sodium carbonate and 0.1 g of sodium peroxide, mix thoroughly, and cover the mixture with an additional 1 g of sodium carbonate. Cover the crucible with a platinum cover, fuse the mixture over a blast burner (Note 13), and allow the melt to cool. Transfer the crucible and contents to a 400-ml (covered) beaker containing approximately 100 ml of water, and heat gently to disintegrate the melt. Remove the crucible and cover after washing them thoroughly with hot water, and boil the solution for at least 10 minutes to destroy the residual peroxide (Note 7). Filter the resulting solution (Whatman No. 40 paper) into a 200-ml volumetric flask, and wash the beaker, paper, and precipitate thoroughly with hot 1% sodium carbonate solution. Discard the paper and precipitate (Note 14). Dilute the filtrate to volume with water and, depending on the amount of vanadium present, proceed with the determination of chromium as described in Procedures A(a) or A(b).

Notes

1. Glassware should be cleaned with hot 25% hydrochloric acid, and then washed thoroughly with distilled water. Chromic acid cleaning solution should not be employed.

2. A solution of diphenylcarbazide in water-free, reagent-quality acetone may be kept for months without appreciable discolouration or loss of chromium sensitivity. The solution should be discarded when it becomes brown[4].

3. Incomplete complex formation, resulting from the possible reduction of chromium (VI) by reducing impurities in the reagents (i.e., water and sulphuric acid) employed, is counteracted by carrying the solutions employed for the preparation of the calibration curve through the oxidation procedure.

4. Because of possible variations in different batches of s-diphenylcarbazide, a new calibration curve should be drawn up for each new batch.

5. The formation of the chromium-diphenylcarbazide complex is almost instantaneous, but the absorbance of the solution slowly decreases on standing because of the slight instability of the complex[1]. Because an initial standing period of approximately 10 minutes is required to eliminate or minimize interference from small amounts of vanadium during subsequent sample analysis, it is recommended

that the absorbance of both the sample and calibration solutions be measured within 10-20 minutes after the addition of diphenylcarbazide solution to counteract error from "fading". Consequently, the diphenylcarbazide solution should be added only to the number of solutions that can be conveniently handled in the above time interval.

6. Crucibles made of ingot iron should be employed. Ordinary iron crucibles may contain significant amounts of chromium.

7. Because peroxide reduces chromium (VI) to the trivalent state in acid solution, the residual peroxide must be destroyed by boiling before an aliquot of the subsequent filtrate is acidified. Boiling for 10 minutes is usually sufficient for solutions containing iron, manganese, or other active decomposition catalysts (e.g., nickel); at least 30 minutes is required if these elements are absent[5]. If any colour due to permanganate ion is observed after the 10-minute boiling period, add 1 ml of ethyl alcohol to reduce permanganate and boil the solution for an additional 10 minutes[3].

8. Litmus paper can be employed as indicator during the neutralization procedure, but it should be removed from the solution before the subsequent oxidation of chromium.

9. Because the last traces of peroxide are difficult to remove by boiling the alkaline solution (Note 7), re-oxidation of the aliquot portion of the filtrate, after acidification, ensures that all of the chromium is present in the hexavalent state prior to complex formation with diphenylcarbazide[5].

10. Methyl orange indicator (0.02% w/v aqueous solution) may be added to the sample and blank solutions and the pH adjustment made by adding the acid solution, by drops, until the colour of the indicator just changes from a pure yellow. The indicator will be destroyed during the subsequent oxidation procedure[1,3].

11. One ml of 0.25% 8-hydroxyquinoline solution is sufficient to complex 0.2-0.3 mg of vanadium[1]. The excess of the reagent is eliminated from the solution during the subsequent chloroform extraction procedure by co-extraction with the vanadium complex. Molybdenum and uranium are also co-extracted under these conditions. Tungsten forms an 8-hydroxyquinoline compound which is not appreciably soluble in chloroform; the precipitate gathers at the chloroform-water interface and interferes by preventing the coalescence of the chloroform droplets after shaking[2].

12 Ignition of the sample oxidizes any reducing substances which could attack the platinum crucible during the subsequent fusion procedure[3].

13. To minimize attack on the platinum crucible by sodium peroxide, the fusion should not be prolonged unnecessarily.

14. Before discarding the paper and precipitate, dissolve the precipitate with dilute (10%) hydrochloric acid. Any black, gritty acid-insoluble residue remaining on the paper at this stage is probably chromite, and should not be discarded. It should be decomposed, after ignition of the paper, by a second fusion with sodium carbonate and sodium peroxide, and the subsequent filtrate should be added to the initial filtrate[3].

Calculations

$$\%Cr_2O_3 = 1.461 \times \%\ Cr$$

Other applications

Using the appropriate fusion procedure, this method can probably be employed to determine chromium in clay, shale, limestone, dolomite, and titanium ores and mill products.

References

1. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 392-401 (1959).

2. Idem, Ind. Eng. Chem., Anal. Ed., 8, 336 (1936).

3. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 457-461 (1968).

4. P.F. Urone, Anal. Chem., 27, 1354 (1955).

5. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 8, pp 324-327 (1963).

DETERMINATION OF COPPER IN ORES AND MILL PRODUCTS BY THE CUPROINE METHOD

Principle

Copper is determined by spectrophotometric measurement, at 545 nm, of the absorbance of the purple 1:2 copper (I)-2,2′-biquinoline (Cuproine) complex, after extraction of the complex into n-amyl alcohol from a weakly acid (pH 6.5-7.0) tartaric acid medium containing hydroxylamine hydrochloride as reductant[1]. The molar absorptivity of the complex in n-amyl alcohol, at 545 nm, is 6.25×10^3 l. mole^{-1}. cm^{-1}.

Outline

The sample is decomposed with hydrochloric, nitric, and sulphuric acids, and the solution is evaporated to dryness. The salts are dissolved in dilute hydrochloric acid, and acid-insoluble material is removed by filtration. The resulting filtrate is analyzed for copper.

Discussion of interferences

Other metal ions do not interfere in the determination of copper with Cuproine because they do not form coloured complexes that are soluble in n-amyl alcohol[1-4]. The extraction procedure eliminates interference from coloured ions (chromium, nickel, cobalt, and vanadium). Tartaric acid complexes and prevents iron and various other elements (e.g., aluminum, titanium, and chromium) from precipitating as their hydrous oxides at the pH employed for the extraction of the copper complex. Silver and mercury precipitate as the chlorides during the initial preparation of the sample solution, but these substances are removed by the preliminary filtration procedure[1].

Range

The method is suitable for samples containing approximately 0.002 to 10% of copper, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard copper solution (1 ml = 0.2 mg of copper). Dissolve 0.1000 g of pure copper metal in 10 ml of 50% nitric acid. Add 10 ml of 50% sulphuric acid, evaporate the solution to fumes of sulphur trioxide, cool, and dilute to 500 ml with water. Dilute 10 ml of this stock solution to 200 ml with water (1 ml = 10 µg of copper).

Cuproine solution, 0.02% w/v in peroxide-free n-amyl alcohol.

Hydroxylamine hydrochloride solution, 10% w/v. Prepare a fresh solution every 5 days.

Tartaric acid solution, 10% w/v.

Ammonium hydroxide, 50% v/v.

Sulphuric acid, 50% v/v.

Hydrochloric acid wash solution, 1% v/v.

Calibration curve

To five 100-ml beakers, add, by burette, 1, 2.5, 5, 7.5, and 10 ml, respectively, of the dilute standard 10 µg/ml copper solution, and dilute each solution to approximately 10 ml with water. Add 10 ml of water to a sixth beaker; this constitutes the blank. Ad 5 ml each of 10% hydroxylamine hydrochloride and 10% tartaric acid solutions to each beaker and, using a pH meter, adjust the pH of each solution to 6.5-7.0 with 50% ammonium hydroxide.

Transfer the resulting solutions to 60-ml separatory funnels, marked at approximately 40 ml, and dilute to the mark with water (Note 1). By pipette, add 10 ml of 0.02% Cuproine-n-amyl alcohol solution to each funnel, stopper, and shake for 1-2 minutes. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layer. Drain the n-amyl alcohol extracts into dry 15-ml centrifuge tubes, and centrifuge for 1 minute. Determine the absorbance of each copper-Cuproine extract (Note 2), at 545 nm, against the blank as the reference solution, using 1-cm cells. Plot µg of copper vs. absorbance.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.2-2.5 g of powdered sample, depending on the expected copper content, to a 250-ml beaker, and add 20 ml of concentrated hydrochloric acid. Boil for approximately 10 minutes, then add 10 ml of concentrated nitric acid and 15 ml of 50% sulphuric acid, and evaporate the solution to dryness. Cool, add 5 ml of concentrated hydrochloric acid, dilute to approximately 40 ml with water, and boil the solution for approximately 15 minutes. Filter the resulting solution (Whatman No. 40 paper) into a volumetric flask of appropriate size (100-1000 ml), and wash the beaker, paper, and residue (Note 3) thoroughly with 1% hydrochloric acid. Cool the filtrate to room temperature, dilute to volume with water and mix.

Transfer a 5-10-ml aliquot of both the sample and blank solutions to 100-ml beakers, add 5 ml each of 10% hydroxylamine hydrochloride and tartaric acid solutions, and proceed with the pH adjustment and the extraction of copper as described above. Measure the absorbance of the sample extract against the reagent blank extract, and determine the copper content of the aliquot by reference to the calibration curve.

Notes

1. The volume of the aqueous phase before extraction should be kept relatively constant to eliminate volume changes in the extract resulting from the partial solubility of n-amyl alcohol in water (i.e., 2.19% by weight at 25°C).

2. The absorbance of the n-amyl alcohol extract of the copper-Cuproine complex remains constant for at least 1 week[1].

3. If the residue is suspected to contain copper, proceed as follows[1]: *Transfer the residue quantitatively to the filter paper, and transfer the paper and contents to a 50-ml porcelain crucible. Burn off the paper at a low temperature, and ignite at approximately 600°C. Fuse the residue with a small amount of sodium peroxide, cool, and transfer the crucible and contents to a 250-ml beaker. Add 50 ml of water, boil to dissolve the melt, and remove the crucible after washing it thoroughly with hot water. Neutralize the solution approximately with concentrated hydrochloric acid and, if necessary, concentrate it by evaporation. Filter the solution, and add the resulting filtrate to the initial filtrate, then proceed as described.*

Other applications

This method can be employed to determine copper in cast iron, steel, aluminum alloys, zinc-base alloys, bauxite, and clay[1]. It is also applicable to carbonate rocks, and to acid-soluble silicate rocks and minerals, and shale if hydrofluoric acid is employed in the decomposition procedure[5].

References

1. R.J. Guest, Anal. Chem., 25, 1484 (1953).
2. J.G. Breckenridge, R.W. Lewis and L. Quick, Can. J. Research, B17, 258 (1939).
3. J. Hoste, Anal. Chim. Acta, 4, 23 (1950).
4. J. Hoste, J. Eeckhout and J.Gillis, ibid., 9, 263 (1953).
5. J.P. Riley and P. Sinhaseni, Analyst, 83, 299 (1958).

DETERMINATION OF IRON IN QUARTZITE, SANDSTONE AND SILICA SAND BY THE 1, 10-PHENANTHROLINE METHOD

Principle

Iron is determined by spectrophotometric measurement, at 510 nm, of the absorbance of the reddish-amber 1:3 iron (II) - 1,10- phenanthroline complex, formed at approximately pH 6 in a sodium acetate medium containing hydroxylamine hydrochloride as reductant[1-3]. The molar absorptivity of the complex, at 510 nm, is 1.11 x 10^4 l. mole^{-1}.cm^{-1} [4].

Outline

The sample is decomposed with hydrofluoric and perchloric acids. The solution is evaporated to dryness to remove silica and excess acids, and the salts are dissolved in dilute hydrochloric acid. The resulting solution is analyzed for iron.

Discussion of interferences

Coloured ions [chromium (III) and (VI)], and ions that form soluble coloured complexes [nickel, cobalt, and copper (I)] and slightly soluble colourless complexes with 1,10- phenanthroline [cadmium, mercury (I), mercury (II), and zinc] interfere in this method. The approximate maximum amount of these ions that can be present during complex formation without producing appreciable error in the iron result is as follows: chromium (III) or chromium (VI) (1 mg), nickel (0.1 mg), cobalt (0.5 mg), copper (I) (0.005 mg), cadmium (0.5 mg), mercury (I) (0.5 mg), mercury (II) (0.05 mg), and zinc (0.5 mg).

Silver, bismuth, beryllium, and more than approximately 1.5 mg of antimony (III) interfere because of the formation of precipitates[1]. Phosphate ion, when present in conjunction with aluminum (and probably titanium, and zirconium), causes low results because of the co-precipitation of ferric phosphate with aluminum phosphate[2]. Up to approximately 1 mg of phosphate alone, as pyro- or orthophosphate, does not interfere if approximately 1 hour is allowed for the formation of the iron complex[2].

Moderate amounts of arsenic (III) and arsenic (V) (25 mg), lead (25 mg), manganese (II) (10 mg), molybdenum (VI) (5 mg), and uranium (VI) (5 mg), and small amounts of tin (II) (0.5 mg), tin (IV) (1 mg), zirconium (0.5 mg), vanadium (V) (1 mg), and tungsten (VI) (0.25 mg) do not interfere[1,3].

Range

The method is suitable for samples containing approximately 0.001 to 5% of iron.

Reagents

Standard iron solution (1 ml = 0.2 mg of iron). Dissolve 0.1000 g of high-purity iron metal by heating with 20 ml of concentrated hydrochloric acid, cool, and dilute to 500 ml with water. Dilute 10 ml of this stock solution to 200 ml with water (1 ml = 10 µg of iron).

1,10-Phenanthroline solution, 0.25 % w/v. Dissolve 0.25 g of 1,10-phenanthroline monohydrate in approximately 75 ml of warm water, cool, and dilute to 100 ml.

Hydroxylamine hydrochloride solution, 10% w/v. Prepare fresh as required.

Sodium acetate buffer solution, 50% w/v.

Calibration curves

To nine 50-ml volumetric flasks, add, by burette, 1, 2, 3, 4, 5, 10, 15, 20, and 25 ml, respectively, of the dilute standard 10 µg/ml iron solution, and dilute each solution to approximately 35 ml with water. Add 35 ml of water to a tenth flask; this constitutes the blank. Add 1 ml of 10% hydroxylamine hydrochloride solution, 2 ml of 0.25% 1,10-phenanthroline solution, and 3 ml of 50% sodium acetate solution to each flask, in succession. Mix after each addition, dilute to volume with water, and allow the solution to stand for approximately 10 minutes to complete the complex formation. Determine the absorbance of each of the first five iron-1,10-phenanthroline solutions, at 510 nm, against the blank as the reference solution, using 5-cm cells. Determine the absorbance of each of the last seven solutions in a similar manner, using 1-cm cells. Plot µg of iron vs. absorbance for each series of measurements.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.2 g of powdered sample to a 100-ml platinum dish, and add 10 ml of concentrated hydrofluoric acid. Allow the mixture to digest at room temperature for approximately 30 minutes, then add 5 ml of concentrated perchloric acid and evaporate the solution to fumes of perchloric acid. Cool, add 5 ml each of water and concentrated hydrofluoric acid. Evaporate the solution to fumes again and, if necessary, repeat the addition of water and hydrofluoric acid and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water and, without baking, gently evaporate the solution to dryness. Add 2-3 drops of concentrated hydrochloric acid and approximately 15 ml of water to the residue, and heat gently to dissolve the salts.

If the sample contains 250 µg or less of iron, transfer both the sample and blank solutions to 50-ml volumetric flasks, dilute to approximately 35 ml with water, and proceed with the formation of the iron (II)-1,10-phenanthroline complex (Notes 1 and 2) as described above. Measure the absorbance of the sample solution against the reagent blank solution, using either 1- or 5-cm cells as required, and determine the iron content of the sample solution by reference to the appropriate calibration curve.

If the sample contains more than 250 µg of iron, transfer both the sample and blank solutions to volumetric flasks of appropriate size (50-200 ml), dilute to volume with water and mix. Transfer a 5-25-ml aliquot of both solutions to 50-ml volumetric flasks, and proceed with the complex formation and subsequent determination of the iron content of the aliquot as described above.

Notes

1. The formation of the iron (II)-1,10-phenanthroline complex may be incomplete if an appreciable amount of concentrated hydrochloric acid is employed to dissolve the residue obtained after evaporation of the sample solution to dryness. Complete complex formation can be obtained by adjusting the pH (using a pH meter) of the solution to approximately 6 by the addition of more sodium acetate solution or, depending on the amount of hydrochloric acid present, by adjusting the pH of the solution to approximately 4 with dilute ammonium hydroxide, prior to the addition of the recommended amount of sodium acetate solution.

2. If the sample contains an appreciable amount of pyrophosphate or orthophosphate ion, a standing period of approximately 1 hour is required for complete formation of the iron (II) complex.

Calculations

$$\%Fe_2O_3 = 1.430 \times \% Fe$$

Other applications

In the absence of phosphate, this method can be employed to determine iron in acid-soluble silicate rocks and minerals, and carbonate rocks.

References

1. W.B. Fortune and M.G. Mellon, Ind. Eng. Chem., Anal. Ed., 10, 60 (1938).

2. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 537-542 (1959).

3. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 2, pp 295-296 (1962).

4. M.L. Moss, M.G. Mellon and G. Frederick Smith, Ind. Eng. Chem., Anal. Ed., 14, 931 (1942).

DETERMINATION OF MANGANESE IN ORES AND MILL PRODUCTS, AND ACID-SOLUBLE SILICATE ROCKS AND MINERALS BY THE PERMANGANATE METHOD

Principle

Manganese is determined by spectrophotometric measurement, at 545 nm, of the absorbance of the purple permanganate ion, formed, according to the reaction

$$2Mn^{+2} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+,$$

in a 2M nitric-0.7 M phosphoric acid medium in the presence of sodium or potassium periodate as oxidant[1,2]. The molar absorptivity of the permanganate ion, at 545 nm, is $2.33 \times 10^3 l.mole^{-1}.cm^{-1}$ [1].

Outline

Ores and mill products that are tungsten-free or contain only small amounts of tungsten are decomposed with hydrochloric, nitric, and perchloric acids. Samples containing large amounts of tungsten are decomposed with the above acids and phosphoric acid. The solution is evaporated to fumes of perchloric acid to oxidize and/or volatilize various sample components, and the acid-insoluble material is ultimately separated by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate and the melt is dissolved in the initial filtrate. The resulting solution is ultimately analyzed for manganese.

Silicate rocks and minerals are decomposed with nitric, hydrofluoric, and perchloric acids. The solution is evaporated to fumes of perchloric acid to remove silica and excess hydrofluoric acid, and the salts are dissolved in water. The resulting solution is analyzed for manganese.

Discussion of interferences

Interference from chromium (III), iron (II), vanadium (IV), organic material, and other ions that reduce sodium periodate or permanganate ion [e.g., chloride, sulphite, nitrite, arsenic (III), and antimony (III)] is eliminated during sample decomposition by the oxidation and/or volatilization of these elements or substances by evaporation with nitric and perchloric acids[3]. Interference from coloured ions [chromium (VI), vanadium (V), copper (II), nickel, cobalt, uranium (VI), and cerium (IV)] is avoided by employing either a portion of the oxidized sample solution in which the permanganate ion has been reduced (i.e., de-colourized) by the addition of sodium nitrite, or an identical aliquot of the sample solution, not treated with sodium periodate, as the reference solution[1]. Phosphoric acid eliminates interference from iron (III) by forming a colourless ferric phosphate complex. This reagent also prevents the precipitation of manganese iodates and periodates during the oxidation procedure, and maintains tungsten in solution during sample decomposition[1,2]. Tin and zirconium interfere by producing a turbid solution, and by precipitating as the phosphate, respectively[3].

Range

The method is suitable for silicate rocks and minerals containing more than approximately 0.005% of manganese, and for ores and mill products containing approximately 0.02 to 10% of manganese. Material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard manganese solution (1 ml = 0.1 mg of manganese). Dissolve 0.1000 g of pure manganese metal in 10 ml of 50% nitric acid, boil the solution to remove oxides of nitrogen, cool, and dilute to 1 litre with water.

Sodium periodate solution, 3% w/v. (Note 1).

Sodium nitrite solution, 5% w/v. Prepare fresh as required.

Hydrogen peroxide, 3% w/v. Dilute 10 ml of 30% hydrogen peroxide to 100 ml with water.

Phosphoric acid, 50% v/v.

Sulphuric acid, 50% v/v.

Calibration curves

Add 13 ml of concentrated nitric acid and 10 ml of 50% phosphoric acid to each of eight 250-ml beakers; then, by burette, add to the last seven beakers 1, 2, 3, 5, 10, 15, and 20 ml, respectively, of the standard 0.1 mg/ml manganese solution. The contents of the first beaker constitute the blank. Dilute the contents of each beaker to approximately 60 ml with water, and add 10 ml of 3% sodium periodate solution. Cover the beakers, heat to the boiling point, and maintain the solutions at, or slightly below the boiling point for approximately 10 minutes to ensure the complete oxidation of manganese (II) to manganese (VII) (Note 2). Cool to room temperature, transfer the resulting solutions to 100-ml volumetric flasks, dilute to volume with water and mix. Determine the absorbance of each of the first three permanganate solutions, at 545 nm (Note 3), against the blank as the reference solution, using 5-cm cells. Determine the absorbance of each of the last six solutions in a similar manner, using 1-cm cells. Plot mg of manganese vs. absorbance for each series of measurements.

Procedures

A - Ores and mill products

(a) Low tungsten content

Transfer 0.4-2 g of powdered sample, depending on the expected manganese content, to a 250-ml beaker, add 30 ml of concentrated hydrochloric acid, cover the beaker, and heat gently, without boiling, for approximately 30 minutes. Add 5 ml of concentrated nitric acid and 20 ml of concentrated perchloric acid, evaporate the solution to fumes of perchloric acid, and continue fuming for approximately 10 minutes (Note 4). Cool, add 50 ml of water, and heat gently to dissolve the soluble salts (Note 5). Filter the resulting solution (Whatman No. 42 paper) into a 250-ml beaker, transfer the residue quantitatively to the filter paper, and wash the beaker, paper, and residue thoroughly with hot water to remove perchlorates.

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 800°C. Cool the crucible, add 1 ml of concentrated nitric acid, 1 ml of 50% sulphuric acid, and 5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the resulting solution to dryness to remove silica and excess sulphuric acid. Fuse the residue with 1-2 g of sodium carbonate, allow the melt to cool, then transfer the crucible and contents to the beaker containing the initial filtrate. When dissolution of the melt is complete, remove the crucible after washing it thoroughly with hot water, and evaporate the solution to fumes of perchloric acid. Add approximately 30 ml of water, and heat gently to dissolve the salts. Cool the solution to room temperature, transfer it to a 100-ml volumetric flask, dilute to volume with water and mix.

Transfer two identical 5-25-ml aliquots of the resulting solution to 250-ml beakers, and add 13 ml of concentrated nitric acid and 10 ml of 50% phosphoric acid. Dilute the solutions to approximately 60 ml with water, then, omitting the addition of sodium periodate solution to one solution, proceed with the oxidation of manganese in the other solution as described above. Measure the absorbance of the coloured sample solution against the non-oxidized solution as the reference solution, using 1- or 5-cm cells as required, and determine the manganese content of the aliquot by reference to the appropriate calibration curve (Note 6).

Alternatively, manganese can be determined, after oxidation of a single aliquot of the sample solution, as follows:

Transfer a portion of the oxidized sample solution to a dry 50-ml beaker, and carefully add 5% sodium nitrite solution, by drops, until 1 drop in excess completely discharges the purple colour of the permanganate ion. Measure the absorbance of the coloured solution against the de-colourized solution as the reference solution (Notes 7 and 8).

(b) High tungsten content

Transfer 0.4-2 g of powdered sample to a 250-ml beaker, and add 20 ml each of concentrated phosphoric, perchloric, and hydrochloric acids, and 10 ml of concentrated nitric acid. Cover the beaker, heat gently for approximately 30 minutes, then evaporate the solution to fumes of perchloric acid, and continue fuming for approximately 10 minutes. Cool, add 50 ml of water, heat gently to dissolve the soluble salts, then proceed with the filtration, ignition, and subsequent treatment of the residue and the resulting solution as described above.

Transfer two identical 5-25-ml aliquots of the sample solution to 250-ml beakers, and add 13 ml of concentrated nitric acid and sufficient 50% phosphoric acid so that approximately 5 ml of the concentrated acid are present. Dilute the solutions to approximately 60 ml with water, and proceed with the oxidation and subsequent determination of manganese as described above (Note 9).

B - Acid-soluble silicate rocks and minerals

(a) Manganese content 0.10% or less

Transfer 2 g of powdered sample to a 100-ml platinum dish, and add 10-15 ml of concentrated hydrofluoric acid. Allow the mixture to digest at room temperature for approximately 30 minutes, then add 10 ml each of concentrated nitric and perchloric acids, and evaporate the solution to fumes of perchloric acid. Cool, add 10 ml each of water and concentrated hydrofluoric acid. Evaporate the solution to fumes again and, if necessary, repeat the addition of water and hydrofluoric acid and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water, and evaporate the solution until approximately 2-3 ml of perchloric acid remain. Add 10-15 ml of water, heat gently to dissolve the salts, filter, if necessary, and transfer the solution to a 250-ml beaker. If necessary, evaporate the resulting solution to approximately 35 ml, add 13 ml of concentrated nitric acid and 10 ml of 50% phosphoric acid, and proceed with the oxidation and subsequent determination of manganese as described in Procedure A (a), using a portion of the coloured solution that has been reduced with sodium nitrite as the reference solution.

(b) Manganese content greater than 0.10%

Decompose 0.4-2 g of sample, depending on the expected manganese content, by the method described above. Slowly evaporate the solution to copious fumes of perchloric acid to ensure the complete removal of hydrofluoric acid, then dissolve the salts in 10-15 ml of water. Transfer the solution to a 100-ml volumetric flask, dilute to volume with water and mix.

Transfer two identical 5-25-ml aliquots of the resulting solution, or a single aliquot if the sodium nitrite method of preparing the reference solution is employed, to 250-ml beakers. Add 13 ml of concentrated nitric acid and 10 ml of 50% phosphoric acid, dilute the solution(s) to approximately 60 ml with water, and proceed with the formation of permanganate ion, and the subsequent determination of manganese as described in Procedure A (a).

Notes

1. If sodium periodate is not available, a hot 3% w/v solution of potassium periodate (less soluble than the sodium salt), or 0.3 g of the solid reagent, may be employed.

2. Manganese (II) is completely oxidized to permanganate in 1-2 minutes at the boiling point of the solution, or in 20-30 minutes at approximately 90°C. At temperatures lower than 90°C, the time required for complete oxidation, particularly with small amounts of manganese, becomes excessive[1,4].

3. Although the permanganate ion exhibits a slightly more intense absorption band at 526 nm than at 545 nm, the latter band is recommended for spectrophotometric measurement, when a

"narrow-band" spectrophotometer (band width of 10 nm or less) is employed, to minimize the background absorbance of the coloured chromium (VI) ion. The absorbance of chromate ion is approximately 70% less at 545 nm than at 526 nm[1,4].

4. When the sample has been dissolved, it must be fumed strongly with perchloric acid to ensure the complete oxidation of elements other than manganese, particularly chromium and vanadium. The validity of the reference solution depends upon prior oxidation of these elements before the periodate oxidation of manganese. If an appreciable amount of chromium is present in the sample, most of it should be removed by volatilization as chromyl chloride. This can be accomplished by the repeated addition of small increments of concentrated hydrochloric acid to the solution, followed by evaporation of the solution to fumes of perchloric acid[1,4].

5. If some manganese has separated as manganese dioxide at this point, add 2-3 drops of 3% hydrogen peroxide to dissolve the brown dioxide, then boil the solution for approximately 5 minutes to remove excess hydrogen peroxide.

6. The reagents employed normally do not contain manganese, or contain insufficient manganese to necessitate a correction for a reagent blank. However, if the presence of manganese is suspected, the appropriate correction can be made by carrying a blank through the same procedure as the sample.

7. Absorbance measurements should be made within approximately 15 minutes after the preparation of the reference solution, because re-oxidation of manganese occurs on standing[1].

8. In general, the previously described method of preparing the reference solution is recommended, because it ensures that the measurement is related to only the permanganate ions (Note 9)[1,4].

9. A duplicate aliquot of the sample solution, not treated with sodium periodate, is recommended as the reference solution for samples containing tungsten. The sodium nitrite method has been found to yield high results for manganese in the presence of tungsten, presumably because of some additional "bleaching" effect[1].

Calculations

$$\%MnO = 1.291 \times \%\ Mn$$

Other applications

The methods described in Procedures A (a) and A (b) can be employed to determine manganese in iron, steel, and ferrous and non-ferrous alloys[1,2,4]. The methods described in Procedures B (a) and B (b) are applicable to carbonate rocks, clay, and shale.

References

1. M.D. Cooper, Anal. Chem., 25, 411 (1953).

2. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 608-616 (1959).

3. J.P. Mehlig, Ind. Eng. Chem., Anal. Ed., 11, 274 (1939).

4. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 7, pp 480-484 (1961).

DETERMINATION OF MERCURY IN TETRAHEDRITE-BEARING ORES AND MILL PRODUCTS BY THE DITHIZONE METHOD

Principle

This method[1,2] is a modification of that developed by Friedeberg[3], and is based on the extraction of mercury, as the primary mercury (II)-diphenylthiocarbazone (dithizone) complex into chloroform, at pH 2, from an ethylenediaminetetra-acetic acid (EDTA) medium. Mercury is determined by spectrophotometric measurement, at 495 nm, of the absorbance of the orange-yellow extract[4].

Outline

The sample is decomposed with hydrochloric and nitric acids at room temperature, and insoluble material is removed by filtration. The resulting filtrate is analyzed for mercury.

Discussion of interferences

Dithizone forms coloured complexes with numerous elements in dilute acid media, but only the complexes that are formed with mercury (I), mercury (II), copper (I), copper (II), silver, palladium (II), platinum (II), gold (III), and possibly bismuth are extracted into chloroform in the pH range 1-3[3,5,6]. Platinum, palladium, and gold interfere in this method. Silver is only partly extracted in the presence of chloride ion[3,6], and bismuth and the major portion of copper are prevented from reacting by complexing them with EDTA[3]. Interference from small amounts of uncomplexed copper and silver, which are co-extracted with the mercury, is eliminated, together with the excess dithizone, by stripping the respective violet-red and yellow complexes from the chloroform extract with 9 M ammonium hydroxide[2,4].

Compounds that oxidize dithizone (e.g., potassium permanganate and hydrogen peroxide) must be absent, or must be reduced prior to the extraction of mercury[5].

Range

The method is suitable for samples containing approximately 0.002 to 1.5% of mercury.

Reagents

Standard mercury solution (1 ml = 1 mg of mercury). Dissolve 0.5399 g of pure, dry mercuric oxide in 30 ml of concentrated nitric acid, and dilute to 1 litre with water (Note 1). Dilute 10 ml of this stock solution to 1 litre with water (1 ml = 10 µg of mercury). Prepare fresh as required.

Dithizone solution, 0.0024% w/v in peroxide-free chloroform. Prepare a fresh solution daily (Note 2), and store in a dark container in a cool place.

Potassium permanganate solution, 1.5% w/v.

Ethylenediaminetetra-acetic acid (EDTA) solution, 5% w/v. Dissolve 25 g of the reagent in 500 ml of 20% ammonium hydroxide. Store in a polyethylene bottle.

Sulphuric acid, 5% v/v.

Ammonium hydroxide wash solution, 9 M. Dilute 600 ml of concentrated ammonium hydroxide to 1 litre with water. Store in a polyethylene bottle.

Ammonium hydroxide, 20% v/v.

Sulphurous acid solution. Water saturated with sulphur dioxide. Prepare a fresh solution daily.

Nitric acid wash solution, 10% v/v.

Chloroform (peroxide-free).

Calibration curve

To four 600-ml beakers, add, by burette, 2.5, 5, 10, and 15 ml, respectively, of the dilute standard 10 µg/ml mercury solution, and dilute each solution to approximately 100 ml with water. Add 100 ml of water to a fifth beaker; this constitutes the blank. Add 25 ml of 5% sulphuric acid, 10 ml of 1.5% potassium permanganate solution (Note 3), 10 ml of sulphurous acid solution, and 20 ml of 5% EDTA solution to each beaker, in succession, and mix thoroughly after each addition. Using a pH meter, adjust the pH of each solution to 2.0 ± 0.1 with 20% ammonium hydroxide, and cool the resulting solutions to room temperature.

Transfer the solutions to 500-ml separatory funnels, add 10 ml of peroxide-free chloroform, stopper, and shake for 30 seconds (Note 4). Allow several minutes for the layers to separate, then carefully drain off and discard the chloroform layer. By pipette or burette, add 50 ml of 0.0024% dithizone-chloroform solution to each funnel (Note 5), stopper, shake for 1 minute, and allow the layers to separate. Transfer the chloroform layer to a second separatory funnel (Note 6), add 50 ml of 9 M ammonium hydroxide, shake for 30 seconds, and allow the layers to separate. Wash the chloroform layer two more times by shaking first with a fresh 50-ml portion of 9 M ammonium hydroxide, then with 25 ml of water. Allow the layers to separate, then insert a wad of cotton-wool into the stem of the funnel and drain a portion of the chloroform extract into a 1-cm cell (Note 7). Determine the absorbance of each extract, at 495 nm, against chloroform as the reference solution (Note 5). Correct the absorbance value obtained for each mercury-dithizone extract by subtracting that obtained for the blank extract. Plot µg of mercury vs. absorbance.

Procedure

In this procedure a reagent blank is carried along with the samples.

Depending on the expected mercury content, transfer 0.5-1 g of sample, ground to at least minus 65 mesh (Note 8), to a 500-ml Erlenmeyer flask, and moisten with several ml of water. Add 20 ml of concentrated hydrochloric acid, cover the flask and, without shaking, allow the mixture to stand at room temperature for 24 hours (Note 9). Add 20 ml of concentrated nitric acid, allow the mixture to stand for a further 24 hours, then add 50 ml of water and some dry paper pulp. Filter the solution (Whatman No. 40 paper) into a 500-ml volumetric flask, and wash the beaker, paper, and residue thoroughly with 10% nitric acid and water. Discard the paper and residue. Dilute the filtrate to volume with water and mix.

Transfer a 10-100-ml aliquot of both the blank and sample solutions to 600-ml beakers, dilute the solutions to 100 ml with water, if necessary, then proceed with the oxidation and extraction of mercury, and the subsequent measurement of the absorbance as described above. Correct the absorbance value obtained for the sample extract by subtracting that obtained for the blank extract, and determine the mercury content of the aliquot by reference to the calibration curve.

Notes

1. Care must be taken to prevent mercury contamination from utensils, and from the air and dust in the laboratory. Because mercury is adsorbed on glass, stock solutions that are more than 1 week old should not be employed, and dilute standard solutions should be prepared just before use. Glassware should be washed with concentrated nitric acid and water before use[6,7].

2. Oxidizing agents oxidize dithizone to diphenylthiocarbadiazone, and solutions of the reagent decompose relatively rapidly when exposed to strong light and moderate temperatures. Consequently, the dithizone solution should be prepared fresh as required, or once a day with peroxide-free chloroform[5,6].

3. Potassium permanganate is added at this stage to ensure that all of the mercury present is in the divalent state. The excess permanganate is destroyed by the subsequent addition of sulphurous acid solution.

4. By this procedure, the aqueous phase is saturated with chloroform before the extraction of the mercury-dithizone complex.

5. Because mercury (II) dithizonate undergoes photochemical decomposition when exposed to strong light, the extraction should be carried out in subdued daylight or artificial light, and the absorbance of the extract should be measured as soon as possible after extraction[4].

6. By siphoning off the upper aqueous layer instead of transferring the chloroform layer to a second funnel, the three subsequent washing stages can be quickly performed in the original separatory funnel.

7. Alternatively, the extracts may be centrifuged to remove water.

8. Complete decomposition of mercury sulphides may not be obtained by the described procedure if the sample is in a coarser state[1].

9. Most of the matrix material dissolves during the preliminary treatment of the sample with hydrochloric acid. Free chlorine, produced by the subsequent addition of nitric acid, oxidizes and dissolves any remaining mercury sulphides. Loss of mercury, by volatilization, will occur if the sample solution is heated at any stage during the decomposition procedure[2].

Other applications

This method can be employed to determine mercury in zinc metal and zinc concentrates[2].

References

1. J.C. Hole, "Determination of Mercury in a Tetrahedrite-Bearing Ore", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Investigation Report IR 68-7, February (1968).
2. L.G. Ripley, "The Spectrophotometric Determination of Mercury in a Zinc Concentrate", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Internal Report MS 66-60, August (1966).
3. H. Friedeberg, Anal. Chem., 27, 305 (1955).
4. F.L. Kozelka, ibid., 19, 494 (1947).
5. J. Starý, "The Solvent Extraction of Metal Chelates", The MacMillan Company, New York, pp 136 -150 (1964).
6. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 621-639 (1959).
7. W.L. Miller and L.E. Wachter, Anal. Chem., 10, 1312 (1950).

DETERMINATION OF MOLYBDENUM IN ORES AND MILL PRODUCTS BY THE THIOCYANATE METHOD

Principle

Molybdenum is determined by spectrophotometric measurement, at 460 nm, of the absorbance of the amber 1:5 molybdenum (V)-thiocyanate complex, formed in an approximately 2 M perchloric acid-citrate medium in the presence of stannous chloride as reductant[1,2].

Outline

The sample is decomposed with hydrochloric, nitric, and perchloric acids, and the solution is evaporated to fumes of perchloric acid to dehydrate silica. Iron and certain interfering elements are subsequently precipitated as the hydrous oxides with sodium hydroxide, and separated from molybdenum by filtration. After dissolution of the precipitate, the hydrous oxides are re-precipitated to recover occluded molybdenum, and the filtrate is combined with the initial filtrate. The resulting solution is ultimately analyzed for molybdenum.

Discussion of interferences

Tungsten, titanium, vanadium, rhenium, platinum, palladium, and rhodium form coloured thiocyanate complexes, chromium forms a reduced coloured compound, and copper forms an insoluble thiocyanate under the conditions employed for the formation of the molybdenum complex[2-6]. Interference from tungsten is eliminated by complexing it with ammonium citrate[2,3,5]. Copper, titanium, iron, certain coloured ions (cobalt, and nickel) some platinum, palladium, and rhodium, and various other ions that may be present in ores and mill products (e.g., zirconium, thorium, uranium, niobium, tantalum, manganese, and cadmium) are separated from molybdenum, prior to complex formation, by precipitation as the hydrous oxides with sodium hydroxide[7]. Rhenium and chromium can be separated from molybdenum by volatilization as the heptoxide and chromyl chloride, respectively, from a hydrochloric-perchloric acid medium.

Moderate amounts of aluminum, arsenic, antimony, bismuth, beryllium, zinc, silica, and phosphate do not interfere[2,6]. Up to approximately 1 mg of vanadium, and trace amounts (less than approximately 100 μg) of platinum, palladium, and rhodium do not produce appreciable error in the molybdenum result[2,6].

Range

The method is suitable for samples containing approximately 0.005 to 4% of molybdenum, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard molybdenum solution (1 ml = 0.2 mg of molybdenum). Dissolve 0.3000 g of pure molybdenum trioxide in 5 ml of 40% sodium hydroxide solution, add approximately 25 ml of water and, using litmus paper, neutralize the solution approximately with concentrated hydrochloric acid. Add several drops in excess, and dilute the resulting solution to 1 litre with water (Note 1). Dilute 25 ml of this stock solution to 200 ml with water (1 ml = 25 μg of molybdenum).

Sodium thiocyanate solution, 50% w/v. Filter the solution, if necessary.

Ammonium citrate solution, 50% w/v. Filter the solution, if necessary.

Stannous chloride solution, 20% w/v. Dissolve 40 g of stannous chloride dihydrate in 50 ml of concentrated hydrochloric acid, and dilute to 200 ml with water. Prepare a fresh solution every week.

Ferric sulphate solution, 20% w/v. Dissolve 20 g of the anhydrous reagent in approximately 75 ml of hot water, cool, and dilute to 100 ml.

Sodium hydroxide solution, 40% w/v. Store in a polyethylene bottle.

Sodium hydroxide wash solution, 0.5% w/v. Prepare fresh as required by appropriate dilution of the 40% solution.

Calibration curves

Add 2 ml of 50% ammonium citrate solution to each of nine 50-ml volumetric flasks; then, by burette, add to the last eight flasks 0.5, 1, 2, 3, 4, 8, 12, and 16 ml, respectively, of the dilute standard 25 µg/ml molybdenum solution. The contents of the first flask constitute the blank. Dilute the contents of each flask to approximately 20 ml with water, add 9 ml of concentrated perchloric acid, and cool the solutions to room temperature. Add 2 ml of 20% ferric sulphate solution (Note 2), 2 ml of 50% sodium thiocyanate solution (Note 3), and 9 ml of 20% stannous chloride solution, to each solution, in succession, and mix thoroughly after each addition. Dilute each solution to volume with water, mix, and allow the solutions to stand for approximately 40 minutes to ensure the complete reduction of iron and complete complex formation (Note 4). Determine the absorbance of each of the first four molybdenum-thiocyanate solutions, at 460 nm, against the blank as the reference solution, using 5-cm cells. Determine the absorbance of each of the last six solutions in a similar manner, using 1-cm cells. Plot µg of molybdenum vs. absorbance for each series of measurements.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.4-1 g of powdered sample, depending on the expected molybdenum content, to a 400-ml beaker, and moisten with several ml of water. Add 10 ml of concentrated hydrochloric acid, boil the solution for approximately 5 minutes, then add 10 ml of concentrated nitric acid and continue boiling until the evolution of brown oxides of nitrogen ceases. Add 7 ml of concentrated perchloric acid, evaporate the solution to fumes of perchloric acid, and continue fuming for approximately 5 minutes to dehydrate the silica (Notes 5 and 6). Cool, add 75 ml of water, and heat gently to dissolve the soluble salts.

Cool to room temperature and, using litmus paper, neutralize the solution approximately with 40% sodium hydroxide solution. Add 1 ml in excess (Note 7), and boil the solution for several minutes to coagulate the resulting hydrous oxide precipitate (Note 8). Filter the solution (Whatman No. 40 paper) into a 400-ml beaker, and wash the beaker, paper and precipitate thoroughly with hot 0.5% sodium hydroxide solution.

Using a jet of hot water, transfer the bulk of the precipitate to the original beaker, and add sufficient concentrated hydrochloric acid to dissolve the precipitate and to provide a small excess. Again add 40% sodium hydroxide solution until the solution is nearly neutral, and re-precipitate the hydrous oxides as described above. Filter the solution through the same filter paper, and wash the beaker, paper, and precipitate as described above. Collect the filtrate and washings in the beaker containing the initial filtrate, and discard the paper and precipitate. Using litmus paper, neutralize the combined filtrates approximately with concentrated hydrochloric acid, and add several drops in excess. If necessary, evaporate the solution (Note 9) to approximately 160 ml, cool, and transfer it to a 200-ml volumetric flask. Dilute the solution to volume with water and mix.

Transfer a 5-20-ml aliquot of both the blank and sample solutions to 50-ml volumetric flasks, add 2 ml of 50% ammonium citrate solution, and proceed with the formation of the molybdenum-thiocyanate complex as described above (Note 10). Measure the absorbance of the sample solution against the reagent blank solution, using 1- or 5-cm cells as required, and determine the molybdenum content of the aliquot by reference to the appropriate calibration curve.

Notes

1. Molybdenum solutions, prepared as described, are stable for 2-3 weeks. On prolonged standing, the solution deposits insoluble molybdenum compounds[2].

2. Some iron must be present in the solution during the formation of the molybdenum (V)-thiocyanate complex when stannous chloride is employed as the reducing agent[8]. In the absence of iron only about 65% of the molybdenum present reacts with thiocyanate to form a coloured complex. The formation of the complexes, $Mo_2^{+3}[Mo^{+5}O(CNS)_5]_3$ and $Fe^{+2}[Mo^{+5}O(CNS)_5]$ in the absence and presence of iron, respectively, has been postulated[9]. A more probable explanation involves the possible effect of iron on the reduction of molybdenum (VI) by stannous chloride, which, on the basis of the above complexes, appears to produce both molybdenum (V) and molybdenum (III) in the absence of iron, and molybdenum (V) alone in the presence of iron[10].

3. The deep red iron (III)-thiocyanate complex which forms at this stage is destroyed by the stannous chloride during the subsequent reduction step. Potassium thiocyanate should not be substituted for sodium thiocyanate in this method because of the relative insolubility of the potassium perchlorate that is formed in perchloric acid media. This compound may precipitate during complex formation and occlude molybdenum[10].

4. The molybdenum-thiocyanate complex that is formed under these conditions is stable for at least 2 hours.

5. If the sample contains rhenium and/or chromium, these elements can be volatilized as the heptoxide and chromyl chloride, respectively, at this stage, by the repeated addition of small amounts of concentrated hydrochloric acid, and subsequent evaporation of the solution to fumes of perchloric acid.

6. Any insoluble yellow hydrated tungsten trioxide that separates at this stage will be re-dissolved during the subsequent treatment of the solution with sodium hydroxide.

7. Copper may not be completely precipitated as the hydrous oxide if the concentration of sodium hydroxide is greater than approximately 1%[7].

8. Any acid-insoluble material (e.g., silica) initially present in the sample solution is removed with the hydrous oxide precipitate during the subsequent filtration procedure.

9. If the sample contains an appreciable amount of tungsten, the solution may become cloudy, or some tungsten trioxide may precipitate during evaporation. If this occurs, add sufficient 40% sodium hydroxide solution to clarify the hot solution, then cool, and reneutralize the solution as described.

10. If the separation of copper is incomplete (Note 7), cuprous thiocyanate may precipitate during complex formation. Small amounts of the white precipitate can be removed by centrifuging the solution before measuring the absorbance of the molybdenum-thiocyanate complex.

Calculations

$\%MoS_2 = 1.669 \times \%\ Mo$

$\%MoO_3 = 1.500 \times \%\ Mo$

Other applications

This method can be employed to determine molybdenum in steel[1,3,4,10]. It is also applicable to silicate rocks and minerals, and to phosphate rocks if the sample is decomposed by fusion with sodium carbonate, or if hydrofluoric acid is employed in the acid-decomposition procedure[10].

References

1. H. Cox and A.A. Pollitt, J. Soc. Chem. Ind., 63, 375 (1944).
2. F.S. Grimaldi and R.C. Wells, Ind. Eng. Chem., Anal. Ed., 15, 315 (1943).
3. M. Kapron and P.L. Hehman, ibid., 17, 573 (1945).

4. L.J. Wrangell, E.C. Bernam, D.F. Kuemmel and O. Perkins, Anal. Chem., 27, 1966 (1955).

5. R.P. Hope, ibid., 29, 1053 (1957).

6. J.O. Hibbits, W.F. Davis, M.R. Menke and S. Kallmann, Talanta, 4, 104 (1960).

7. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 81-83 (1938).

8. C.E. Crouthamel and C.E. Johnson, Anal. Chem., 26, 1284 (1954).

9. A.T. Dick and J.B. Bingley, Australian J. Exptl. Biol. Med. Sci., 25, 193 (1947); Nature, 158, 516 (1946).

10. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 644-664 (1959).

DETERMINATION OF NICKEL IN ORES AND MILL PRODUCTS, AND ACID-SOLUBLE SILICATE ROCKS AND MINERALS BY THE DIMETHYLGLYOXIME METHOD

Principle

Nickel is determined by spectrophotometric measurement, at 530 nm, of the absorbance of the reddish-brown nickel (III)- or nickel (IV)-dimethylglyoxime complex, formed in an ammoniacal ammonium citrate medium in the presence of iodine as oxidant[1,2].

Outline

The sample is decomposed with hydrochloric, nitric, hydrofluoric, and perchloric acids. The solution is evaporated to fumes of perchloric acid to remove silica and excess hydrofluoric acid, and the salts are dissolved in water. Platinum, palladium, and/or large amounts of copper, if present, are precipitated as the sulphides in a dilute hydrochloric acid medium and separated from nickel by filtration. The resulting filtrate, or the preceding solution, if the above interfering elements are absent, is ultimately analyzed for nickel.

Discussion of interferences

Copper (II), platinum (II), and palladium (II) interfere in the determination of nickel because they form coloured complexes with dimethylglyoxime under the conditions employed for the formation of the nickel complex[2-4]. Iron (II), bismuth, and cobalt (II) also form coloured complexes in ammoniacal media[3]. Small amounts of copper and cobalt (equivalent to the amount of nickel present) do not cause significant error in the nickel result.

Interference from platinum, palladium, and large amounts of copper is avoided by separating these elements, and various other elements of the copper and arsenic groups (bismuth, molybdenum, rhenium, germanium, gold, cadmium, mercury, silver, tin, lead, arsenic, antimony, selenium, and tellurium) from nickel by precipitation as the sulphides with hydrogen sulphide from a 0.4-0.5 M hydrochloric acid medium[5].

Interference from iron (II), initially present in the sample, or produced during the hydrogen sulphide separation procedure, is avoided by oxidizing it to the trivalent state with nitric acid during sample decomposition, or after the hydrogen sulphide separation. Interference from bismuth is eliminated by complexing it with ammonium citrate[3]. This reagent also maintains iron (III), and various other elements that form hydrous oxides in ammoniacal media (aluminum, cerium, zirconium, and titanium) in solution during complex formation.

Chromium, vanadium, and cerium react with iodine or iodide ion, but this interference can be avoided by employing a sufficient excess of oxidant[2]. Interference from coloured ions [iron (III), chromium, and vanadium] is eliminated by employing an identical aliquot of the sample solution, not treated with dimethylglyoxime, as the reference solution. Moderate amounts of tungsten and molybdenum[4], and small amounts of manganese (approximately equal to the amount of nickel present) do not interfere[1].

Note: For samples containing large amounts of manganese, copper, cobalt, molybdenum, tungsten, and elements that readily hydrolyze in acid solution (e.g., niobium, tantalum, titanium, and zirconium) the Spectrophotometric-Dimethylglyoxime-Chloroform Extraction Method for nickel (p 73) is recommended.

Range

The method is suitable for samples containing approximately 0.01 to 10% of nickel.

Reagents

Standard nickel solution (1 ml = 0.5 mg of nickel). Dissolve 3.3647 g of nickel ammonium sulphate hexahydrate [$NiSO_4.(NH_4)_2SO_4.6H_2O$] in water, and dilute to 1 litre. Dilute 25 ml of this stock solution to 500 ml with water (1 ml = 25 μg of nickel).

Dimethylglyoxime solution, 0.1% w/v. Dissolve 1 g of dimethylglyoxime in 500 ml of concentrated ammonium hydroxide and dilute to 1 litre with water.

Iodine solution, 0.1 M. Dissolve 12.5 g of potassium iodide in approximately 25 ml of water, and add 6.35 g of dry re-sublimed iodine. Stir the solution until the iodine has completely dissolved, and dilute to 500 ml with water. Store in a brown glass-stoppered bottle in a cool, dark place.

Ammonium citrate solution, 50% w/v. Dissolve 500 g of citric acid in approximately 300 ml of water, add 500 ml of concentrated ammonium hydroxide, and dilute to 1 litre with water.

Ammonium hydroxide, 50% v/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% hydrochloric acid saturated with hydrogen sulphide.

Calibration curve

To six 100-ml volumetric flasks, add, by burette, 2, 4, 8, 12, 16 and 20 ml, respectively, of the dilute standard 25 μg/ml nickel solution, and dilute each solution to approximately 55 ml with water. Add 55 ml of water to a seventh flask; this constitutes the blank. Add 1 ml of concentrated perchloric acid, 10 ml of 50% ammonium citrate solution, and 1 ml of 0.1 M iodine solution to each flask, in succession, and mix thoroughly after each addition. Add 20 ml of 0.1% dimethylglyoxime solution to the blank and the first of the nickel solutions. Dilute each solution to volume with water and mix. Allow the solutions to stand for several minutes to complete the complex formation (Note 1), then determine the absorbance of the nickel-dimethylglyoxime solution, at 530 nm, (Note 2), against the blank as the reference solution, using 2-cm cells. Proceed, in a similar manner, with the formation of the nickel-dimethylglyoxime complex and the subsequent determination of the absorbance for each succeeding nickel solution, and plot μg of nickel vs. absorbance.

Procedures

Platinum, palladium, and large amounts of copper absent

Transfer 0.25-2 g of powdered sample, depending on the expected nickel content, to a 250-ml Teflon beaker, and add 10 ml each of concentrated hydrochloric, nitric, and hydrofluoric acids. Cover the beaker with a Teflon cover, and heat gently until the decomposition of the sample is complete. Remove the cover, add 10 ml of concentrated perchloric acid, and evaporate the solution to strong fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and again evaporate the solution to fumes. Add approximately 40 ml of water, and heat gently for several minutes to dissolve the soluble salts. If necessary, filter the solution (Whatman No. 30 paper and paper pulp) into a volumetric flask of appropriate size (100-250 ml), dilute to volume with water and mix.

Transfer two identical 5-20-ml aliquots of the resulting solution to 100-ml volumetric flasks, dilute to approximately 55 ml with water, and add 10 ml of 50% ammonium citrate solution and 1 ml of 0.1 M iodine solution. Add 20 ml of 50% ammonium hydroxide to one solution, and proceed with the formation of the nickel-dimethylglyoxime complex (Note 3) in the other solution as described above. Measure the absorbance of the coloured sample solution against the solution to which no dimethylglyoxime solution was added, and determine the nickel content of the aliquot by reference to the calibration curve (Note 4).

Platinum, palladium, and/or large amounts of copper present

Following sample decomposition and dissolution of the salts in water as described above, transfer the solution to a 400-ml pyrex beaker, and evaporate it to dryness. Add 5-7 ml of concentrated hydrochloric acid and approximately 25 ml of water to the residue, heat gently to dissolve the salts, and dilute the solution to approximately 150 ml with hot water. Pass hydrogen sulphide through the solution for 15 minutes, allow it to stand for about

30 minutes, then filter the solution (Whatman No. 32 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hydrogen sulphide wash solution. Discard the paper and precipitate, and boil the filtrate to expel hydrogen sulphide. Add 10 ml each of concentrated nitric and perchloric acids, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and again evaporate the solution to fumes. Add approximately 40 ml of water, and heat gently to dissolve the salts. Transfer the solution to a volumetric flask of appropriate size, dilute to volume with water, mix, and proceed with the determination of nickel as described above.

Notes

1. Absorbance measurements should be made within approximately 5 minutes after the addition of dimethylglyoxime solution and dilution to volume because the nickel complex formed under these conditions is unstable and either decomposes or partly changes to a different complex on standing[4].

2. Although the oxidized nickel-dimethylglyoxime complex exhibits an intense absorption band at 445 nm, a less intense band at 530 nm is employed for spectrophotometric measurement to minimize the background absorbance due to ferric iron[1].

3. If the sample contains an appreciable amount of cerium, chromium, or vanadium, more than 1 ml of 0.1 M iodine solution may be required for complete oxidation of the nickel; this is indicated by the yellow colour of the blank solution after the addition of 50% ammonium hydroxide. Although a large excess of oxidant interferes by destroying dimethylglyoxime[4], up to approximately 4 ml may be added, before the addition of the ammonium hydroxide or ammoniacal dimethylglyoxime solution, without causing appreciable error in the nickel result.

4. The reagents employed normally do not contain nickel, or contain insufficient nickel to necessitate a correction for a reagent blank. However, if the presence of nickel is suspected, the appropriate correction can be made by carrying a blank through the same procedure as the sample.

Other applications

This method can be employed to determine nickel in steels[1].

References

1. M.D. Cooper, Anal. Chem., 23, 875 (1951).

2. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Mines Branch Monograph 866, Method No. Ni-2, Part III, April (1958).

3. H. Diehl, "The Applications of the Dioximes to Analytical Chemistry", G. Frederick Smith Chemical Co., Columbus, Ohio, pp 35-46 (1940).

4. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 665-681 (1959).

5. G.E.F Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, 54 (1938).

DETERMINATION OF NICKEL IN ORES AND MILL PRODUCTS, AND ACID-SOLUBLE SILICATE ROCKS AND MINERALS BY THE DIMETHYLGLYOXIME-CHLOROFORM EXTRACTION METHOD

Principle

This method[1,2] is based on the extraction of nickel, as nickel (II) dimethylglyoximate, into chloroform[3], at pH 6.5, from a tartrate-sodium thiosulphate medium. Nickel is determined by spectrophotometric measurement, at 370 nm, of the absorbance of the yellow extract[4,5]. The molar absorptivity of the complex, at 370 nm, is $3.44 \times 10^3 l.mole^{-1}.cm^{-1}$.

Outline

The sample is decomposed with hydrochloric, nitric, hydrofluoric, and sulphuric acids, and the solution is evaporated to fumes of sulphur trioxide to remove silica. Niobium, tantalum, titanium, zirconium, and various other elements that may be present (iron, bismuth, tin, aluminum, and tungsten) are complexed with hydrofluoric acid and ammonium tartrate. The excess hydrofluoric acid is complexed with boric acid. The resulting solution is ultimately analyzed for nickel.

Discussion of interferences

Copper (II), cobalt (II), platinum (II), palladium (II), and gold (III) form coloured dimethylglyoxime complexes that are partly soluble in chloroform, and co-extract, to some extent, with the nickel[6]. Interference from copper (II) is avoided by complexing it with sodium thiosulphate. This reagent also complexes lead, zinc, cadmium, and silver under the conditions employed for the extraction of nickel[2]. Interference from cobalt is eliminated by stripping the brown complex from the chloroform extract with dilute ammonium hydroxide[1]. Platinum, palladium, and gold can be separated from nickel, prior to the extraction of nickel (II) dimethylglyoximate, by precipitation as the sulphides from an approximately 0.5 M sulphuric acid medium.

Iron (II) and bismuth also form coloured complexes with dimethylglyoxime, but iron is oxidized to the trivalent state during sample decomposition, and bismuth is complexed with ammonium tartrate during the preparation of the sample solution[1]. The following elements, when present separately in the aliquot taken for analysis, in at least the amounts shown, do not interfere: magnesium (500 mg), niobium (250 mg), tantalum (250 mg), molybdenum (VI) (250 mg), tungsten (VI) (250 mg), iron (III) (250 mg), aluminum (125 mg), thorium (125 mg), manganese (II) (100 mg), zinc (100 mg), zirconium (100 mg), tin (IV) (100 mg), silver (100 mg), cadmium (100 mg), copper (II) (50 mg), cerium (IV) (40 mg), cobalt (II) (25 mg), lead (10 mg), chromium (III) (5 mg), and vanadium (V) (5 mg)[1,2].

Range

The method is suitable for samples containing approximately 0.001 to 5% of nickel.

Reagents

Standard nickel solution (1 ml = 0.5 mg of nickel). Prepare as described in the Spectrophotometric-Dimethylglyoxime Method for nickel (p 69). Dilute 10 ml of this stock solution to 500 ml with water (1 ml = 10 µg of nickel).

Dimethylglyoxime solution, 1% w/v in ethyl alcohol.

Ammonium tartrate solution, 25% w/v.

Sodium thiosulphate solution, 50% w/v. Dissolve 250 g of the reagent in hot water, cool, and dilute to 500 ml.

Boric acid solution, 5% w/v. Dissolve 50 g of the reagent in approximately 800 ml of hot water, cool, and dilute to 1 litre.

Sulphuric acid, 50% v/v.

Ammonium hydroxide, 10% and 2% v/v.

Hydrochloric acid, 10% v/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% sulphuric acid saturated with hydrogen sulphide.

Chloroform. Analytical reagent-grade.

Ethyl alcohol, 95%.

Calibration curve

Add 5 ml of 25% ammonium tartrate solution to each of five 150-ml beakers; then, by burette, add to the last four beakers 2.5, 5, 7.5, and 10 ml, respectively, of the dilute standard 10 µg/ml nickel solution. Dilute the contents of each beaker to approximately 50 ml with water. The contents of the first beaker constitute the blank. Add 5 ml of 50% sodium thiosulphate solution to each of the resulting solutions and, using a pH meter, adjust the pH of each solution to 6.5 ± 0.1 with 2% ammonium hydroxide.

Transfer the solutions to 125-ml separatory funnels, after washing the stem of each funnel with ethyl alcohol to remove water droplets, and dilute to approximately 100 ml with water. Add 5 ml of chloroform and 3 ml of 1% dimethylglyoxime solution to each funnel, stopper, and shake for 2 minutes. Allow 5 minutes for the layers to separate, then carefully (Note 1) drain the chloroform extract into a dry 25-ml volumetric flask. Re-extract the solution by shaking for 1 minute with 3 ml of chloroform, and then for 30 seconds with 2 ml of chloroform. Combine these extracts with the first, dilute to volume with ethyl alcohol (Note 2) and mix. Determine the absorbance of each chloroform-ethyl alcohol solution of nickel (II) dimethylglyoximate, at 370 nm, against the blank as the reference solution, using 5-cm cells. Plot µg of nickel vs. absorbance.

Procedures

In these procedures a reagent blank is carried along with the samples.

Cobalt absent

Transfer 0.2-0.5 g of powdered sample, depending on the expected nickel content, to a 250-ml Teflon beaker, and add 20 ml of 50% sulphuric acid and 5 ml each of concentrated hydrochloric, nitric, and hydrofluoric acids. Cover the beaker with a Teflon cover, heat gently until the decomposition of the sample is complete, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water and evaporate the solution until approximately 4 ml of sulphuric acid remain. Cool, add approximately 15 ml of water, mix thoroughly (Notes 3 and 4), then add 1 ml of concentrated hydrofluoric acid and 10 ml of 25% ammonium tartrate solution, and heat gently, without boiling, until the solution is clear (Note 5). Add 20 ml of 5% boric acid solution, and allow the solution to stand for approximately 20 minutes. Filter the solution (Whatman No. 42 paper), if lead sulphate is present, into a volumetric flask of appropriate size (100-1000 ml), dilute to volume with water and mix.

Transfer a 10-50-ml aliquot of both the sample and blank solutions to 150-ml beakers, and dilute to approximately 50 ml with water. Using a pH meter, adjust the pH of the solutions to 4.5-5.0 (Note 6) using concentrated and 10% ammonium hydroxide as required. Add 5 ml of 50% sodium thiosulphate solution (Note 7), mix, and immediately adjust the pH to 6.5 ± 0.1 (Note 8) using, in succession, concentrated, 10%, and 2% ammonium hydroxide, and/or concentrated and 10% hydrochloric acid as required. Transfer the solutions to 125-ml separatory funnels, dilute to approximately 100 ml with water, and proceed with the extraction of nickel dimethylglyoximate as described above (Note 9). Measure the absorbance of the sample solution against the reagent blank solution, and determine the nickel content of the aliquot by reference to the calibration curve.

Cobalt present

Following pH adjustment and dilution of the resulting sample and blank solutions to 100 ml with water in 125-ml separatory funnels, add sufficient 1% dimethylglyoxime solution to react with the cobalt and to provide an excess for the nickel (Note 10). Extract the nickel dimethylglyoximate as described above and drain the chloroform extracts into 60-ml separatory funnels, after washing the stem of each funnel with ethyl alcohol to remove water droplets. Add 10 ml of 2% ammonium hydroxide to the combined extracts, stopper, and shake for 30 seconds. Allow several minutes for the layers to separate, then drain the chloroform layer into a dry 25-ml volumetric flask. Wash the aqueous layer by shaking for 30 seconds with 1 ml of chloroform, and add this to the combined extracts. Dilute the combined extracts to volume with ethyl alcohol, and determine the nickel content of the aliquot as described above.

Notes

1. Because of the high salt content of the aqueous phase, care must be taken that none of it accompanies the chloroform extract or else the final chloroform-ethyl alcohol solution of nickel dimethylglyoximate will be turbid.

2. Dilution of the combined chloroform extracts with ethyl alcohol removes turbidity caused by the retention of small droplets of water in the organic phase. The absorbance of the chloroform-ethyl alcohol solution of nickel dimethylglyoximate remains constant for at least 24 hours[1].

3. If insoluble hydrous oxides of niobium, tantalum, titanium, or zirconium are not present, as indicated by a clear solution, the subsequent addition of hydrofluoric acid and boric acid solution may be omitted.

4. In the absence of large amounts of tungsten and readily hydrolyzed elements (Note 3), palladium, platinum, and gold, if present, can be separated from nickel at this stage as follows: *Transfer the solution to a 400-ml beaker, dilute to approximately 150 ml with hot water, and pass hydrogen sulphide through the resulting solution for approximately 15 minutes. Allow the solution to stand for about 30 minutes, then filter it (Whatman No. 32 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hydrogen sulphide wash solution. Discard the paper and precipitate. Boil the filtrate to expel hydrogen sulphide, add 5 ml of 50% sulphuric acid, and 10 ml of concentrated nitric acid to oxidize iron (II), and evaporate the solution until approximately 4 ml of sulphuric acid remain. Cool, add 15 ml of water and 10 ml of 25% ammonium tartrate solution, transfer the solution to a volumetric flask of appropriate size (100-1000 ml), dilute to volume with water and mix. Using suitable aliquots of the solution, proceed with the pH adjustment and subsequent extraction of nickel as described.*

5. If yellow hydrated tungsten trioxide is present at this stage, add sufficient concentrated ammonium hydroxide to dissolve the precipitate, neutralize the resulting solution approximately with 50% sulphuric acid, and re-acidify it by adding 8 ml in excess.

6. To prevent the precipitation of the hydrous oxide of zinc, the pH of the solution must be less than approximately 5.5 for prior complexation of zinc with sodium thiosulphate[2].

7. Five ml of 50% sodium thiosulphate solution are sufficient to complex either 50 mg of copper or approximately 100 mg of zinc. Up to 10 ml may be employed if larger amounts of these elements are present[2].

8. Nickel (II) dimethylglyoximate is extracted at pH 6.5 because the copper thiosulphate complex is stable at this pH; above pH 7 the complex is unstable[2].

9. Nickel can be stripped from the chloroform phase at this stage by shaking the combined extracts with dilute (0.5-1 M) hydrochloric acid, and then determined by the Spectrophotometric-Dimethylglyoxime Method (p 69). If this method is employed, larger amounts of nickel can be extracted, depending on the solubility of the nickel complex in chloroform (i.e., 35 μg of nickel/ml of chloroform)[7], by using more dimethylglyoxime and chloroform[6].

10. Approximately 4 ml of 1% dimethylglyoxime solution for each 5 mg of cobalt present is sufficient to react with the cobalt and to provide an excess for the nickel. The alcohol content of the solution, resulting from the addition of the dimethylglyoxime solution, should not exceed 35% by volume[6].

Other applications

With modifications in the decomposition procedure, this method can be employed to determine nickel in niobium, tantalum, molybdenum, and tungsten metals[1], brass, bronze, magnesium and aluminum metals and alloys[2], iron and steel[6].

References

1. Elsie M. Penner (Donaldson) and W.R. Inman, Talanta, 10, 997 (1963).
2. Idem, "Determination of Nickel by Spectrophotometric Measurement of the Chloroform Extract of Nickel II Dimethylglyoximate - Application to Brasses, Bronzes, Magnesium and Aluminum Metals and Their Alloys", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB 49, September (1963).
3. E.B. Sandell and R.W. Perlich, Ind. Eng. Chem., Anal. ed., 11, 309 (1939).
4. A.J. Hall and R.S. Young, Analyst, 71, 479 (1946).
5. W. Nielsch, Z. Anal. Chem., 140, 267 (1953).
6. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 665-681 (1959).
7. W. Nielsch, Z. Anal. Chem., 143, 272 (1954).

DETERMINATION OF NIOBIUM IN ROCKS, ORES AND MILL PRODUCTS BY THE THIOCYANATE METHOD

Principle

This method[1,2] is based on the formation of the niobium (V)-thiocyanate complex in a 4 M hydrochloric acid-0.5 M tartaric acid medium, and the subsequent extraction of the yellow complex into ethyl ether. Niobium is determined by spectrophotometric measurement, at 385 nm, of the absorbance of the extract.

Outline

The sample is decomposed by fusion with sodium bisulphate, or by treatment with hydrochloric, hydrofluoric, and phosphoric acids, followed by evaporation of the solution to a paste to remove excess hydrofluoric acid. The melt or paste is dissolved in tartaric acid solution. The resulting solution is analyzed for niobium.

Discussion of interferences

Molybdenum, tungsten, titanium, cobalt, iron (III), vanadium (III), (and possibly bismuth) interfere in this method, if present in large amounts, because they form coloured thiocyanate complexes that are partly or completely co-extracted into the ethyl ether phase[1,3]. Interference from iron (III) (up to 1 mg) is eliminated, after the ether extraction step, by reducing the iron and subsequently destroying the co-extracted red complex, by shaking the extract with stannous chloride solution[1]. Interference from vanadium (up to 0.5 mg) is prevented by extracting the niobium (V) and iron (III) complexes before the addition of stannous chloride. Under these conditions, vanadium remains in the non-reactive pentavalent or tetravalent state[1]. Moderate amounts of tantalum are maintained in solution with tartaric acid, but large amounts can cause low results for niobium because of hydrolysis and subsequent co-precipitation of niobium[3,4]. Small amounts of molybdenum and/or tungsten (equal to the amount of niobium present), and up to approximately 1000 μg of titanium, 200 μg of tantalum, or 100 μg of bismuth can be present in the aliquot taken for analysis without causing appreciable error in the niobium result[1]. Moderate amounts of cobalt do not interfere because the co-extracted blue complex does not absorb at the wavelength employed for the measurement of the absorbance of the niobium complex[3].

Uranium (VI) forms a coloured, ether-insoluble complex under the conditions employed for the formation of the niobium complex[1], but up to approximately 1 mg does not interfere when the sample is decomposed with hydrochloric, hydrofluoric, and phosphoric acids[1,2]. Low results are obtained for niobium, in the presence of uranium, when the sample is decomposed by fusion with sodium bisulphate, presumably because all of the niobium is not converted to the reactive NbO^{+3} or $Nb(OH)_x^{5-x}$ forms when the aliquot taken for analysis is acidified with hydrochloric acid[2,5].

Acids or anions that decompose thiocyanate (e.g., nitric acid and nitrates), and anions, other than tartrate, that form complexes with niobium (e.g., fluoride, citrate, and oxalate) should not be present during complex formation[3].

Range

The method is suitable for samples containing approximately 0.01 to 2% of niobium, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard niobium solution (1 ml = 0.1 mg of niobium). Transfer 0.0286 g of pure niobium pentoxide and 4 g of fused sodium bisulphate to a 30-ml silica or quartz crucible and mix thoroughly. Add 2-3 drops of concentrated sulphuric acid, cover the crucible, and carefully fuse the mixture (to avoid frothing) over an open flame until a clear melt is obtained. Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, and allow the crucible and contents to cool. Transfer the crucible and cover to a 250-ml beaker, add 75 ml of 1 M tartaric acid solution, and heat gently until the melt becomes detached from the crucible. Remove the crucible and cover after washing them thoroughly with 1 M tartaric acid solution and, while stirring, continue heating until a clear solution is obtained. Cool the resulting solution to room temperature, transfer it to a 200-ml volumetric flask, and dilute to volume with 1 M tartaric acid solution (Note 1). Transfer 2-, 5-, 10-, 15-, and 20-ml increments of this stock solution to 100-ml volumetric flasks, add 1-2 ml of concentrated phosphoric acid, and dilute each solution to volume with 1 M tartaric acid solution (1 ml of the resulting solutions = 2, 5, 10, 15, and 20 µg, respectively, of niobium). Prepare fresh as required.

Sodium bisulphate. Fuse an appropriate amount of the reagent in a quartz or silica container, cool, and grind in a mortar.

Ammonium thiocyanate solution, 20% w/v. Prepare fresh as required.

Stannous chloride solution, 10% w/v. Dissolve 10 g of stannous chloride dihydrate in 100 ml of 2 M hydrochloric acid. Prepare a fresh solution every 2 days.

Tartaric acid solution, 1 M. Dissolve 300 g of the reagent in water, and dilute to 2 litres.

Hydrochloric-tartaric acid solution, 9 M and 1 M, respectively. Dissolve 15 g of tartaric acid in 100 ml of 9 M hydrochloric acid.

Hydrochloric acid, 9 M. Dilute 385 ml of concentrated acid to 500 ml with water.

Hydrochloric acid, 2 M. Dilute 86 ml of concentrated acid to 500 ml with water.

Ethyl ether (peroxide-free). Purify just before use by shaking 100 ml with 10 ml of 10% stannous chloride solution.

Calibration curve

Transfer 1-ml aliquots of each of the dilute standard niobium solutions (Note 2) to 60-ml separatory funnels. Transfer an identical aliquot of a corresponding solution, prepared by diluting 1-2 ml of concentrated phosphoric acid to 100 ml with 1 M tartaric acid solution, to another separatory funnel; this constitutes the blank. By pipette, add 5 ml of the 9 M hydrochloric acid-1 M tartaric acid solution and 5 ml of 20% ammonium thiocyanate solution to the funnels containing the blank and the first of the niobium solutions, then, without delay (Note 3), add 5 ml of peroxide-free ethyl ether to each funnel, stopper, and shake for 30 seconds. Allow the layers to separate, drain off and discard the lower aqueous layer, and add 2 ml of 10% stannous chloride solution to the ether layer. Shake for 10 seconds, allow the layers to separate, and again drain off and discard the lower aqueous phase. Repeat the stannous chloride wash of the ether layer two more times, then transfer the ether phase to a 10-ml volumetric flask, dilute to volume with acetone and mix (Note 4). Proceed, in a similar manner, with the formation and extraction of the niobium-thiocyanate complex in each of the remaining solutions. Determine the absorbance of each ether-acetone solution of niobium thiocyanate, at 385 nm, against the blank as the reference solution, using 1-cm cells. Plot µg of niobium vs. absorbance.

Procedures

In these procedures a reagent blank is carried along with the samples.

Acid-decomposition procedure

Transfer 0.2-1 g of powdered sample, depending on the expected niobium content, to a 100-ml platinum dish, and add 1-2 ml of concentrated phosphoric acid and 10 ml each of concentrated hydrochloric and hydrofluoric acids (Note 5). Heat the mixture gently for approximately 30 minutes to decompose siliceous material, then carefully evaporate the solution until only a paste of phosphoric acid remains (Note 6). Wash the contents of the dish into a volumetric flask of appropriate size (100 or 200 ml) with 1 M tartaric acid solution, dilute to volume with the same solution (Notes 7-9) and mix.

Transfer a 1-ml aliquot of both the sample and blank solutions to 60-ml separatory funnels, and proceed with the formation and extraction of the niobium-thiocyanate complex as described above (Note 10). Measure the absorbance of the ether-acetone sample solution against the reagent blank solution, and determine the niobium content of the aliquot by reference to the calibration curve.

Fusion procedure in the absence of uranium

Decompose 0.2 g of sample by fusion with 4 g of fused sodium bisulphate as described above for the preparation of the standard niobium solution. Dissolve the melt in 50 ml of 1 M tartaric acid solution then, depending on the expected niobium content, transfer the resulting solution, without filtering, to a 100- or 200-ml volumetric flask. Dilute the solution to volume with 1 M tartaric acid solution, mix, and proceed with the extraction and subsequent determination of niobium as described above.

Notes

1. Solutions containing niobium should be at least 1 M in tartaric acid to prevent the niobium from hydrolyzing.

2. Because tartaric acid influences the formation of the niobium-thiocyanate complex[3], the preparation of separate dilute standard niobium solutions in 1 M tartaric acid solution, and the utilization of identical 1-ml aliquots of these solutions for calibration purposes, ensures that the tartaric acid concentration remains constant during the formation and extraction of the niobium complex. The extraction and subsequent determination of niobium in sample solutions is carried out under identical conditions.

3. Because thiocyanate polymerizes and rapidly forms coloured decomposition products in strong acid media, the niobium complex should be extracted into ether immediately, or within several minutes after the addition of the ammonium thiocyanate[1,3].

4. Dilution of the ether extract of niobium thiocyanate with an equal volume of acetone stabilizes the extract, presumably by inhibiting the polymerization of co-extracted thiocyanic acid. The absorbance of the resulting ether-acetone solution of niobium thiocyanate remains constant for at least 20 hours[1].

5. In general, the acid decomposition procedure, rather than the fusion procedure, is recommended for sample decomposition. This procedure is more rapid and permits the use of a larger sample when the niobium content is low; also the hydrofluoric acid employed removes silica from the solution and converts all of the niobium to a reactive form[2,5]. When necessary, up to 5 g of sample can be decomposed conveniently by this method. Sulphide minerals such as pyrite and molybdenite are not decomposed by the acid treatment, and consequently, the resulting solution is less contaminated with iron and molybdenum, which interfere in the determination of niobium if present in large amounts[2].

6. Do not fume or evaporate the solution to dryness at this stage. This can result in the formation of niobium compounds that are not readily redissolved in tartaric acid solution.

7. Filtration of the solution is usually not necessary unless large quantities of finely-divided insoluble material are present.

8. Samples containing more than 2% of niobium can be analyzed, with reasonable accuracy, by diluting the initial sample solution to a larger volume, or by diluting a suitable aliquot of the solution to an appropriate volume with 1 M tartaric acid solution.

9. If the sample contains an appreciable amount of tantalum, the tartaric acid solution of the sample should be analyzed for niobium without delay. Partial hydrolysis of tantalum occurs when the solution is allowed to stand. This causes low results for niobium because of the co-precipitation of niobium with the colloidal hydrous tantalum oxide[4].

10. The presence of an excessive amount of molybdenum in the aliquot taken for analysis will be indicated by the amber colour of the extract.

Calculations

$$\%Nb_2O_5 = 1.431 \times \% Nb$$

References

1. F.N. Ward and A.P. Marranzino, Anal. Chem., 27, 1325 (1955).
2. G.H. Faye, Chemistry in Canada, 10, 90 (1958).
3. A.B.H. Lauw-Zechta, S.S. Lord, Jr. and D.N. Hume, Anal. Chem., 24, 1169 (1952).
4. M.N. Bukhsh and D.N. Hume, ibid., 27, 116 (1955).
5. C.E. Crouthamel, B.E. Hjelte and C.E. Johnson, ibid., 27, 507 (1955).

DETERMINATION OF PHOSPHORUS IN IRON ORES AND CONCENTRATES, AND MOLYBDENUM AND TUNGSTEN ORES AND MILL PRODUCTS BY THE PHOSPHOVANADOMOLYBDIC ACID-ISOAMYL ALCOHOL EXTRACTION METHOD

Principle

This method[1] is based on that developed by Elwell and Wilson[2], and involves the formation of phosphovanadomolybdic acid in a 1 M nitric acid-0.005 M ammonium vanadate-0.01 M ammonium molybdate medium, and the subsequent extraction of the yellow mixed heteropoly compound into isoamyl alcohol. Phosphorus is determined by spectrophotometric measurement, at 425 nm, of the absorbance of the yellow extract.

Outline

Iron ores and concentrates are decomposed with hydrochloric acid, and the solution is treated with nitric acid to convert phosphorus to orthophosphate. Silica is dehydrated by evaporation with perchloric acid, and the acid-insoluble material is ultimately removed by filtration and ignited. The silica in the resultant residue is removed by volatilization as silicon tetrafluoride, and the residue is fused with sodium carbonate to convert refractory phosphates (titanium, zirconium, and possibly thorium) to soluble phosphate. The melt is digested in water, and the hydrous oxides of the above elements are removed by filtration. The residual phosphorus in the filtrate is subsequently co-precipitated as ferric phosphate with hydrous ferric oxide, the precipitate is dissolved in dilute hydrochloric acid, and the solution is added to the initial filtrate. The resulting solution is ultimately analyzed for phosphorus.

Following the decomposition of molybdenum and tungsten ores and mill products with nitric, hydrochloric, and sulphuric acids, the separation of phosphorus from molybdenum and tungsten by precipitation as magnesium ammonium phosphate, and the dissolution of the precipitate in dilute nitric acid, as described in the Volumetric-Alkalimetric Method for phosphorus (Procedure B, p 342, Note 27), the resulting solution is ultimately analyzed for phosphorus.

Discussion of interferences

If present in large amounts, bismuth, thorium, hydrochloric, and hydrofluoric acids interfere in the formation of phosphovanadomolybdic acid by inhibiting complex formation; tungsten interferes by forming a heteropoly compound with phosphorus; and titanium, zirconium, and tin interfere by forming insoluble phosphates. Arsenic, silicon, and germanium interfere by forming similar heteropoly vanadomolybdic acid or heteropoly molybdate compounds. Iron (II) and sulphides interfere by either reducing phosphovanadomolybdic acid, or the excess molybdate, to molybdenum blue[3-5].

Interference from iron (II) is eliminated by oxidizing it to the trivalent state with nitric acid during sample decomposition. Silica is removed by volatilization as silicon tetrafluoride, and hydrochloric and hydrofluoric acids, and sulphur compounds (i.e., sulphides) are removed or destroyed by evaporation with perchloric or sulphuric acids. Interference from germanium, tin, and large amounts of arsenic can be avoided by volatilizing these elements as the bromides from a hydrobromic-perchloric or a hydrobromic-sulphuric acid medium. Elements that form insoluble phosphates (titanium, zirconium, and thorium), and various other elements that may be present in the acid-insoluble residue (niobium, and tantalum) are separated from phosphorus as the hydrous oxides, after fusion of the residue with sodium carbonate and digestion of the melt in water. Phosphorus is separated from molybdenum and tungsten, and various other elements that may be present in molybdenum and tungsten ores and mill products (e.g., tin, titanium, vanadium, chromium, bismuth, selenium, tellurium, and zirconium) by precipitating it as magnesium ammonium phosphate from an ammoniacal tartrate medium[5,6].

Chromium (VI), if present during complex formation, causes low results for phosphorus. This interference is avoided by reducing this ion to the trivalent state with sodium sulphite prior to complex formation[2]. The extraction procedure eliminates interference from chromium (III) and other coloured ions [nickel, cobalt, copper, and iron (III)][2]. Up to approximately 1 mg each of thorium and arsenic, and up to 0.25, 5, and 20 mg of zirconium, titanium, and bismuth, respectively, can be present during complex formation without causing appreciable error in the phosphorus result[2-4]. Up to at least 50 mg of aluminum, barium, beryllium, cadmium, calcium, magnesium, manganese (II), mercury (II), uranium (VI), zinc, lead, silver, molybdate, silicate, selenate, and the alkali metals do not interfere[3].

Range

The method is suitable for samples containing approximately 0.002 to 2% of phosphorus.

Reagents

Standard phosphorus solution (1 ml = 50 µg of phosphorus). Dissolve 0.2292 g of anhydrous disodium phosphate (Na_2HPO_4) (dried at 105°C for 1-2 hours) in approximately 200 ml of water, add 100 ml of 20% nitric acid, and dilute to 1 litre with water (Note 1).

Ammonium vanadate-ammonium molybdate solution, 0.2% and 4% w/v, respectively. Dissolve 2 g of ammonium metavanadate (NH_4VO_3) in approximately 300 ml of water, and add 140 ml of concentrated nitric acid. Dissolve 40 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in approximately 400 ml of water, then combine the two solutions. Transfer the resulting solution to a 1-litre volumetric flask, and dilute to volume with water. Prepare a fresh solution every 3 days.

Iron (III) solution, 3% w/v. Dissolve 15 g of high-purity iron metal (phosphorus-free) in 100 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, cool, and dilute the solution to 500 ml with water.

Sodium sulphite solution, 10% w/v. Prepare fresh as required.

Nitric acid, 50% and 20% v/v.

Hydrochloric acid, 50% and 30% v/v.

Sulphuric acid, 3% v/v.

Isoamyl alcohol. Analytical reagent-grade.

Calibration curve

Add 10 ml of 3% iron (III) solution (Note 2) and 20 ml of 50% nitric acid to each of seven 300-ml Erlenmeyer flasks; then, by burette, add to the last six flasks, 1, 2, 4, 6, 8, and 10 ml, respectively, of the standard 50 µg/ml phosphorus solution. The contents of the first flask constitute the blank. Add 7 ml of concentrated perchloric acid to each flask, evaporate the solution to fumes of perchloric acid, and continue fuming for approximately 5 minutes. Cool, add 30 ml of water to dissolve the salts, then add 10 ml of 10% sodium sulphite solution, and boil the solution for approximately 10 minutes or until all of the resulting sulphur dioxide has been expelled. Add 8 ml of 20% nitric acid, boil the solution for an additional 3 minutes (Note 3), then remove the flask from the source of heat. Add 25 ml of 0.2% ammonium vanadate-4% ammonium molybdate solution to the hot solutions, mix, and cool to 15-20°C in a water-bath.

Transfer the resulting solutions to 250-ml separatory funnels, and dilute to approximately 80 ml with water. By pipette, add 50 ml of isoamyl alcohol to each funnel, stopper, and shake for 2 minutes. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layer. Add 10 ml of 3% sulphuric acid to each funnel, and shake for 15 seconds (Note 4). Allow the layers to separate, then drain off and discard the aqueous layer and approximately 3-5 ml of the alcohol layer. Drain a portion of the isoamyl alcohol extracts into 15-ml centrifuge tubes, and centrifuge for 30 seconds (Note 5). Determine the absorbance of each extract (Note 6), at 425 nm, against isoamyl alcohol as the reference solution, using 2-cm cells. Correct the absorbance value obtained for each phosphovanadomolybdic acid extract by subtracting that obtained for the blank extract. Plot µg of phosphorus vs. absorbance.

Procedures

In these procedures a reagent blank is carried along with the samples.

Iron ores and concentrates

Transfer 1 g of powdered sample to a 250-ml beaker, and moisten with several ml of water. Add 20 ml of concentrated hydrochloric acid, and heat gently, without boiling, until the decomposition of acid-soluble material is complete. Add 5 ml of concentrated nitric acid and 7 ml of concentrated perchloric acid, evaporate the solution to fumes of perchloric acid, and continue fuming for approximately 5 minutes to dehydrate the silica. Cool, add 30 ml of water, heat gently to dissolve the soluble salts (Note 7), then filter the resulting solution (Whatman No. 40 paper) into a 300-ml Erlenmeyer flask, and transfer the residue quantitatively to the filter paper. Wash the paper and residue twice with warm 30% hydrochloric acid, then thoroughly with hot water to remove perchlorates. Evaporate the filtrate and washings to approximately 25 ml.

Transfer the paper and residue to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 700°C. Cool the crucible, and add 2 ml of concentrated perchloric acid and 5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess perchloric acid. Fuse the residue with 1-3 g of sodium carbonate, cool, and transfer the crucible and contents to a 250-ml beaker. Add 50 ml of water, heat gently to disintegrate the melt and to dissolve soluble salts, then remove the crucible after washing it thoroughly with hot water. Filter the resulting solution (Whatman No. 40 paper) into a 250-ml beaker, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue. Add 10 ml of concentrated hydrochloric acid to the filtrate, boil the solution for several minutes to expel carbon dioxide, cool, and add 1 ml of 3% iron (III) solution. Neutralize the solution approximately with concentrated ammonium hydroxide to precipitate the hydrous oxide of iron and ferric phosphate, and add approximately 1 ml in excess. Boil the resulting solution for approximately 1 minute to coagulate the precipitate, then filter the solution (Whatman No. 541 paper) and wash the beaker, paper, and precipitate several times with hot water. Discard the filtrate. Dissolve the precipitate, using 10 ml of warm 50% hydrochloric acid, and wash the paper thoroughly with hot water. Collect the solution in the beaker in which the precipitation was carried out, and discard the paper. Add the resulting solution to the initial filtrate (Note 8).

If the sample contains approximately 100 µg or less of phosphorus, evaporate both the sample and blank solutions to fumes of perchloric acid, and fume for 5 minutes. Add 30 ml of water to dissolve the salts, then proceed with the sodium sulphite treatment, the formation and extraction of phosphovanadomolybdic acid, and the subsequent measurement of the absorbance as described above. Correct the absorbance value obtained for the sample extract by subtracting that obtained for the blank extract, and determine the phosphorus content of the sample extract by reference to the calibration curve.

If the sample contains more than 100 µg of phosphorus, transfer both the sample and blank solutions to volumetric flasks of appropriate size (200-1000 ml), dilute to volume with water and mix. Transfer a 25-100-ml aliquot of both solutions to 300-ml Erlenmeyer flasks, and add 3-4 ml of concentrated perchloric acid. Evaporate the solutions to fumes of perchloric acid, and proceed with the complex formation, extraction, and subsequent determination of the phosphorus content of the aliquot as described above.

Molybdenum and tungsten ores and mill products

Following the decomposition of a 1-g sample with nitric, hydrochloric, and sulphuric acids, the separation of phosphorus from molybdenum and tungsten by precipitation as magnesium ammonium phosphate, and the dissolution of the precipitate in dilute nitric acid as described in the Volumetric-Alkalimetric Method for phosphorus (Procedure B, p 342, Note 27), add 7 ml of concentrated perchloric acid and 10 ml of 3% iron (III) solution (Note 9) to both the sample and blank solutions or, depending on the expected phosphorus content of the sample, to suitable aliquots of the solutions as described above. Evaporate the resulting solutions to fumes of perchloric acid, fume for 5 minutes, then proceed with the sodium sulphite treatment, the formation and extraction of phosphovanadomolybdic acid, and the subsequent determination of phosphorus as described above.

Notes

1. All glassware should be cleaned with hot concentrated hydrochloric acid and washed with water to remove any phosphorus-bearing compounds.

2. The addition of iron to the solutions employed for the preparation of the calibration curve is necessary to counteract the effect of iron, contained in samples of iron ore and concentrates, on the formation and subsequent extraction of phosphovanadomolybdic acid. Iron, in large amounts, interferes in this method, to some extent, because of the formation of iron (III) molybdate[2]. However, the iron content of the sample or aliquot taken for analysis can vary considerably without producing appreciable error in the phosphorus result[1].

3. The re-oxidation of any ferrous iron, produced during the preceding treatment with sodium sulphite, is ensured by re-boiling the solution after the addition of nitric acid[2].

4. Co-extracted molybdic acid is partly removed by washing the extracts with 3% sulphuric acid.

5. Alternatively, the extracts may be dried by filtering through a thick wad of cotton-wool into a dry 50- or 100-ml volumetric flask.

6. Absorbance measurements should be made within 20-30 minutes after extraction. The absorbance of the extract slowly decreases on standing because of the slight instability of phosphovanadomolybdic acid in isoamyl alcohol[2].

7. If the sample contains an appreciable amount of manganese, any manganese dioxide that may have precipitated during evaporation of the solution to fumes of perchloric acid may be re-dissolved at this stage by the addition of several crystals of sodium nitrite.

8. If the sample contains tin, germanium, or more than approximately 1 mg of arsenic, proceed as follows:

Evaporate the solution to approximately 30 ml, and add 5-10 ml of concentrated hydrobromic acid. Evaporate the solution to fumes of perchloric acid, wash down the sides of the flask with water, again evaporate to fumes, then proceed as described.
Antimony is also volatilized as the bromide by the above procedure.

9. The calibration curve prepared by extracting phosphorus as phosphovanadomolybdic acid in the presence of iron (Note 2) applies only to the determination of phosphorus in materials containing iron. Consequently, in order to utilize the same calibration curve for the determination of phosphorus in molybdenum and tungsten ores and mill products, iron (III) solution, equivalent to that added to the calibration solutions, must be added to the sample solution or aliquot of the solution, prior to the formation and subsequent extraction of the phosphovanadomolybdic acid.

Calculations

$$\%P_2O_5 = 2.291 \times \%P$$

Other applications

The method described for iron ores and concentrates can be employed to determine phosphorus in iron and steel[2]. It should be applicable to iron ore mill products if iron (III) solution is added to the sample solution or aliquot of the solution, prior to the formation and extraction of the phosphovanadomolybdic acid (Note 9).

References

1. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E278-67T, pp 766-769 (1970).

2. W.T. Elwell and H.N. Wilson, Analyst, 81, 136 (1956).

3. R.E. Kitson and M.G. Mellon, Ind. Eng. Chem., Anal. Ed., 16, 379 (1944).

4. G. Lindley, Anal. Chim. Acta, 25, 334, (1961).

5. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 694-710 (1953).

6. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E31-67, pp 97-98 (1970).

DETERMINATION OF PHOSPHORUS IN ACID-SOLUBLE SILICATE ROCKS AND MINERALS, QUARTZITE, SANDSTONE, SILICA SAND, CARBONATE ROCKS, CLAY, SHALE, BAUXITE, AND PHOSPHATE ROCKS BY THE PHOSPHOVANADOMOLYBDIC ACID METHOD

Principle

This method[1,2] is based on that developed by Kitson and Mellon[3], and involves the formation of the yellow mixed heteropoly complex, phosphovanadomolybdic acid, in a 0.8 M nitric acid - 0.002 M ammonium vanadate-0.008 M ammonium molybdate medium. Phosphorus is determined by spectrophotometric measurement, at 460 nm, of the absorbance of the complex.

Outline

The sample is decomposed with hydrofluoric and nitric acids to remove silica, and to convert phosphorus to the orthophosphate form, respectively. The solution is evaporated to dryness, and the salts are dissolved in dilute nitric acid. Residual fluoride is subsequently complexed with boric acid. The acid-insoluble material is removed by filtration, ignited, and fused with sodium carbonate to convert refractory phosphates (titanium, zirconium, and possibly thorium) to soluble phosphate. The melt is digested in water, and the hydrous oxides of the above elements are removed by filtration. The filtrate is ultimately combined with the initial filtrate. The resulting solution is analyzed for phosphorus.

Discussion of interferences

Large amounts of zirconium, thorium, and titanium interfere in this method because they form insoluble phosphates, but up to approximately 0.25, 1, and 5 mg, respectively, of these elements may be present separately during complex formation without causing appreciable error in the phosphorus result[3,4]. Interference from coloured ions [chromium (III), chromium (VI), iron (III), copper (II), nickel, and cobalt] is avoided by employing an identical aliquot of the sample solution, not treated with ammonium vanadate and ammonium molybdate, as the reference solution[2].

Up to at least 50 mg of aluminum, barium, calcium, magnesium, manganese (II), silicate, alkali metals, beryllium, cadmium, mercury (II), uranium (VI), zinc, lead, silver, molybdate, and selenate do not interfere[3]. Germanium, and more than 1 mg of arsenic interfere because they form similar heteropoly vanadomolybdic acid or heteropoly molybdate compounds[5]. Tungsten interferes by forming a heteropoly compound with phosphorus, and cerium and tin precipitate as phosphates during complex formation[3].

Range

The method is suitable for samples containing more than approximately 0.01% of phosphorus.

Reagents

Standard phosphorus solution (1 ml = 0.2 mg of phosphorus). Dissolve 0.4584 g of anhydrous disodium phosphate (Na_2HPO_4) (dried at 105°C for 1-2 hours) in water (Note 1), dilute to 500 ml, and store in a polyethylene bottle.

Ammonium vanadate solution, 0.25% w/v. Dissolve 2.5 g of ammonium metavanadate (NH_4VO_3) in approximately 500 ml of water, and add 20 ml of concentrated nitric acid. Allow the resulting solution to stand overnight, filter it, if necessary, and dilute to 1 litre with water.

Ammonium molybdate solution, 5% w/v. Dissolve 50 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in approximately 500 ml of warm water. Allow the resulting solution to stand overnight, filter it, if necessary, dilute to 1 litre with water, and store in a polyethylene bottle.

Boric acid solution, 5% w/v. Dissolve 50 g of the reagent in approximately 800 ml of hot water, cool, and dilute to 1 litre.

Nitric acid, 50% v/v. Boil the solution to remove oxides of nitrogen.

Calibration curve

Add 5 ml of concentrated, colourless nitric acid to each of eight 100-ml volumetric flasks; then, by burette, add to the last seven flasks 0.5, 1, 2, 4, 6, 8 and 10 ml, respectively, of the standard 0.2 mg/ml phosphorus solution. The contents of the first flask constitute the blank. Dilute the contents of each flask to approximately 50 ml with water, add 10 ml of 0.25% ammonium vanadate solution, and mix thoroughly. Add 20 ml of 5% ammonium molybdate solution, dilute to volume with water, mix, and allow the solutions to stand at room temperature for approximately 30 minutes (Note 2). Determine the absorbance of each phosphovanadomolybdic acid solution, at 460 nm (Note 3), against the blank as the reference solution, using 2-cm cells. Plot mg of phosphorus vs. absorbance.

Procedures

In these procedures a reagent blank is carried along with the samples.

Acid-soluble silicate rocks and minerals, quartzite, sandstone, silica sand, carbonate rocks, clay, shale, and bauxite

Transfer 1 g of powdered sample (Note 4) to a 100-ml platinum dish, and moisten with approximately 5 ml of water. Cover the dish and slowly add 10 ml of concentrated nitric acid, in small portions, until the decomposition of any carbonates present is complete. Remove the cover, add 10 ml of concentrated hydrofluoric acid, mix by swirling, then at low heat, slowly evaporate the solution to dryness (Note 5). Cool, wash down the sides of the dish with a small amount of water, add 5 ml each of concentrated nitric and hydrofluoric acids, mix, and again evaporate the solution to dryness. Add 20 ml of 50% nitric acid, evaporate the solution to dryness, and heat the resulting residue (Note 5) for approximately 30 minutes to expel volatile fluorides. Cool, add 20 ml of 50% nitrogen oxide-free nitric acid and 10 ml of 5% boric acid solution. Cover the dish with a plastic or Teflon cover, and digest the contents on a hot water-bath until the dissolution of solid material appears to be complete (Note 6). Filter the resulting solution (Whatman No. 40 paper) into a 100-ml volumetric flask, transfer the residue (Note 7) quantitatively to the filter paper, and wash the dish and paper several times with water containing a few drops of concentrated nitric acid.

Transfer the paper and residue to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 700°C. Fuse the residue with 0.5 g of sodium carbonate, cool, and transfer the crucible and contents to a 250-ml beaker. Add approximately 50 ml of water, heat gently to disintegrate the melt and to dissolve soluble salts, then remove the crucible after washing it thoroughly with hot water. Filter the resulting solution (Whatman No. 40 paper) into a 250-ml beaker, and wash the beaker, paper and residue thoroughly with hot water. Discard the paper and residue. Neutralize the filtrate approximately with concentrated nitric acid, add 2-3 drops in excess, and evaporate the solution to approximately 10 ml. Add the resulting solution to the initial filtrate, dilute the combined solution to volume with water and mix.

Transfer two identical 10-40-ml aliquots of both the blank and sample solutions, depending on the expected phosphorus content, to 100-ml volumetric flasks, and add sufficient concentrated, colourless nitric acid so that 5 ml of the concentrated acid are present. Dilute the solutions to approximately 50 ml with water, then, omitting the addition of ammonium vanadate and ammonium molybdate solutions to one aliquot of each solution, proceed with the complex formation as described above. Measure the absorbance of the blank and sample solutions against the corresponding solutions, to which no ammonium vanadate and ammonium molybdate solutions were added. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution, and determine the phosphorus content of the aliquot by reference to the calibration curve.

Phosphate rocks

Decompose 0.5 g of powdered sample (Notes 4 and 7) by the method described above. Dilute the resulting combined solution to 500 ml with water, then transfer two 10-ml aliquots of both the blank and sample solutions to 100-ml volumetric flasks, and add 5 ml of concentrated nitric acid. Dilute the solutions to approximately 50 ml with water, and proceed with the complex formation and subsequent determination of phosphorus as described above.

Notes

1. All glassware should be cleaned with hot concentrated hydrochloric acid and washed with water to remove any phosphorus-bearing compounds

2. Because the absorbance of the phosphovanadomolybdic acid complex varies, to some extent, with temperature[4,6], a standing period of at least 30 minutes at room temperature is recommended to eliminate or minimize this temperature effect. The complex forms within approximately 5 minutes and, after standing for 30 minutes at room temperature, is stable for at least an additional 30 minutes[3].

3. Although the phosphovanadomolybdic acid complex exhibits an intense absorption band at approximately 315 nm[7], a wavelength of 460 nm is employed for spectrophotometric measurement to minimize the background absorbance of the reagents (i.e., ammonium vanadate and ammonium molybdate), ferric iron, and certain other coloured ions (copper and nickel)[2].

4. If much organic material is present in the sample (e.g., clay, shale, and carbonate rocks), it should be ignited at 800-900°C for approximately 30 minutes.

5. Some phosphorus may be lost, presumably by volatilization, if the residue resulting from the evaporation of the sample solution to dryness is heated or baked at temperatures exceeding 250°C[2].

6. Any manganese dioxide (i.e., a brown precipitate) that is present at this stage may be re-dissolved by the addition of several crystals of sodium sulphite. If the solution is turbid because of the presence of hydrous oxides of titanium and/or zirconium, boil it for several minutes to produce a filterable precipitate.

7. If only a small amount, or no residue is present, the subsequent ignition and fusion procedure may be omitted. A white residue should not be discarded because it may contain titanium and/or zirconium phosphates.

Calculations

$$\%P_2O_5 = 2.291 \times \%P$$

References

1. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 384-385, 392-393 (1968).

2. H. Baadsgaard and E.B. Sandell, Anal. Chim. Acta, <u>11</u>, 183 (1954).

3. R.E. Kitson and M.G. Mellon, Ind. Eng. Chem., Anal. Ed., <u>16</u>, 379 (1944).

4. G. Lindley, Anal. Chim. Acta, <u>25</u>, 334 (1961).

5. W.T. Elwell and H.N. Wilson, Analyst, <u>81</u>, 136 (1956).

6. W.M. Murray, Jr., and S.E.Q. Ashley, Ind. Eng. Chem., Anal. Ed., <u>10</u>, 1 (1938).

7. O.B. Michelsen, Anal. Chem., <u>29</u>, 60 (1957).

DETERMINATION OF RHENIUM IN MOLYBDENITE CONCENTRATES BY THE THIOCYANATE METHOD

Principle

Rhenium is determined by spectrophotometric measurement, at 425 nm, of the absorbance of the amber rhenium (V)-thiocyanate complex, formed in a 2.9 M hydrochloric acid-30% acetone medium in the presence of stannous chloride as reductant[1,2].

Outline

The sample is decomposed by fusion with sodium peroxide and sodium carbonate, and the melt is dissolved in water. Molybdenum and certain interfering elements are ultimately separated from rhenium by cupferron-chloroform extraction. The resulting aqueous phase is analyzed for rhenium.

Discussion of interferences

Molybdenum, titanium, vanadium, tungsten, platinum, palladium, rhodium, and gold form coloured thiocyanate complexes; copper forms an insoluble thiocyanate; and selenium and tellurium are reduced to the elemental state under the conditions employed for the formation of the rhenium (V)-thiocyanate complex[3,4].

Interference from molybdenum, titanium, and vanadium is eliminated by separating these elements, and various other elements (e.g., iron, zirconium, tin, antimony, and some copper) from rhenium by chloroform extraction of their cupferron complexes from a 3 M hydrochloric acid medium[4,5]. Platinum, palladium, rhodium, gold, selenium, and tellurium are not separated by this procedure and interfere in this method[3]. Tungsten precipitates as the hydrated oxide during evaporation of the hydrochloric acid solution of the melt, and can be separated from rhenium by filtration. Up to approximately 2 mg of copper do not interfere.

Range

The method is suitable for samples containing approximately 0.003 to 0.12% of rhenium.

Reagents

Standard rhenium solution (1 ml = 0.2 mg of rhenium). Dissolve 0.1441 g of ammonium perrhenate (NH_4ReO_4) in water and dilute to 500 ml. Dilute 25 ml of this stock solution to 200 ml with water (1 ml = 25 μg of rhenium).

Potassium thiocyanate solution, 20% w/v. Prepare fresh as required, and filter the solution, if necessary.

Stannous chloride solution, 10% w/v. Dissolve 10 g of stannous chloride dihydrate in 50 ml of concentrated hydrochloric acid, and dilute to 100 ml with water. Prepare fresh as required.

Cupferron solution, 9% w/v. Prepare fresh as required using only pure white cupferron, and filter the solution, if necessary.

Chloroform. Analytical reagent-grade.

Calibration curve

Add 10 ml of concentrated hydrochloric acid to each of seven 50-ml volumetric flasks; then, by burette, add to the last six flasks 1, 2, 4, 6, 8, and 10 ml, respectively, of the dilute standard 25 μg/ml rhenium solution. The contents of the first flask constitute the blank. Dilute the contents of each flask to exactly 25 ml with water, cool, if necessary, then add 5 ml of 10% stannous chloride solution and 5 ml of 20% potassium thiocyanate solution, and mix thoroughly after each addition. Dilute each solution to volume with acetone (Note 1), mix, and allow the solutions to stand for 15 minutes to complete the complex formation. Determine the absorbance of each rhenium-thiocyanate solution (Note 2), at 425 nm, against the blank as the reference solution, using 2-cm cells. Plot µg of rhenium vs. absorbance.

Procedure

In this procedure a reagent blank is carried through all of the stages of the procedure except the cupferron-chloroform extraction step (Note 3).

Transfer 1 g of powdered sample (Note 4) to a 30-ml zirconium crucible, add 3 g of sodium peroxide and 2 g of sodium carbonate and mix thoroughly. Cautiously fuse the mixture (to avoid spattering) over an open flame, and maintain it in the molten state for several minutes to ensure complete sample decomposition. Allow the melt to cool for approximately 5 minutes, then transfer the crucible and contents to a 400-ml beaker containing 50-60 ml of water. When the subsequent reaction has ceased (Note 5), remove the crucible after washing it thoroughly with hot water, and neutralize the solution approximately with concentrated hydrochloric acid. Add 25 ml in excess, and boil the resulting solution gently to remove the carbon dioxide and hydrogen peroxide formed during the acidification step. Evaporate the solution to approximately 75 ml and cool to room temperature (Note 6).

Transfer the solution to a 250-ml separatory funnel, dilute to approximately 100 ml with water, and cool to about 6°C in an ice-bath. Ad 60 ml of cold 9% cupferron solution, stopper, and shake for 1 minute. Add 50 ml of chloroform, shake for 1 minute, allow several minutes for the layers to separate, then drain off and discard the chloroform layer. Re-extract the solution three more times using, in succession, 25, 15, and 15 ml of chloroform, and shaking for 1 minute each time (Note 7). Filter the aqueous layer (Whatman No. 541 paper) into a 400-ml beaker, heat gently to remove the residual chloroform, then evaporate the solution to approximately 75 ml. Cool the resulting solution to room temperature, transfer it to a 100-ml volumetric flask, dilute to volume with water and mix.

Transfer 20-ml aliquots of both the sample and blank solutions to 50-ml volumetric flasks, add 5 ml of concentrated hydrochloric acid (Note 8), then proceed with the formation of the rhenium-thiocyanate complex as described above. Measure the absorbance of the sample solution against the reagent blank solution, and determine the rhenium content of the aliquot by reference to the calibration curve.

Notes

1. Acetone increases the rate of complex formation and prevents the reduction of rhenium (VII) beyond the pentavalent state[1].

2. The absorbance of the aqueous-acetone solution of rhenium thiocyanate remains constant for at least 2 hours.

3. The cupferron-chloroform extraction step is omitted in the case of the reagent blank to avoid the presence of large amounts of organic material in the resulting solution. Large amounts of un-complexed cupferron are not readily removed by extraction with chloroform.

4. The decomposition of larger samples, which necessitates the use of larger amounts of flux material, is not recommended because of the excessive amount of sodium salts that will be present in the final solution.

5. Any insoluble black material (possibly sulphides of molybdenum) that may be present at this stage can be dissolved by the addition of small portions of 30% hydrogen peroxide.

6. Tungsten, if present, precipitates as the hydrous oxide during evaporation of the sample solution and can be removed at this stage by filtering the solution into the separatory funnel.

7. Continued extraction with chloroform is necessary to remove the major portion of the un-complexed cupferron. The usual method of destroying organic material, by treatment with nitric acid and subsequent evaporation to fumes of sulphur trioxide or perchloric acid, cannot be employed in this method because rhenium volatilizes as the heptoxide under these conditions[3].

8. If smaller aliquots of the sample and blank solutions are taken, sufficient concentrated hydrochloric acid must be added so that approximately 10 ml are present prior to complex formation.

References

1. C.E. Crouthamel, Anal. Chem., 29, 1756 (1957).

2. A.D. Melaven and K.B. Whetsel, ibid., 20, 1209 (1948).

3. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 750-766 (1959).

4. R.J. Meyer and C.L. Rulfs, Anal. Chem., 27, 1387 (1955).

5. J. Starý and E. Hladký, Anal. Chim. Acta, 28, 227 (1963).

DETERMINATION OF SILICON IN IRON ORES BY THE MOLYBDENUM BLUE METHOD

Principle

This method[1] is based on the formation of the yellow, heteropoly β-silico-12-molybdic acid complex in a dilute nitric acid medium, and the subsequent reduction of the complex to the molybdenum blue complex with ascorbic acid in a 0.8 M sulphuric acid medium. Silicon is determined by spectrophotometric measurement, at 600 nm, of the absorbance of the blue reduced complex.

Outline

The sample is decomposed by fusion with sodium tetraborate to convert silica to the reactive monomeric form, and the melt is dissolved in dilute nitric acid. The resulting solution is analyzed for silicon.

Discussion of interferences

Phosphorus (V), arsenic (V), and germanium form similar yellow heteropoly molybdate complexes under the conditions employed for the formation of the yellow β-silicomolybdic acid complex[2,3]. Interference from phosphorus and arsenic is eliminated by the destruction of these complexes with oxalic acid, prior to the reduction of the silicon complex[4]. Germanium is not normally present in iron ores, and small amounts of various other elements that may be present (e.g.,manganese, titanium, zirconium, aluminum, copper, and vanadium) do not interfere[3].

Oxidizing agents [chromium (VI) and hydrogen peroxide] interfere, if present in large amounts, by preventing the reduction of the yellow complex. Hydrogen peroxide also prevents the formation of the yellow complex because it reacts with the molybdate to form an intense yellow peroxy-molybdate complex[2,3]. Reducing agents, other than ascorbic acid, should not be present during or after formation of the yellow complex[2,3].

Range

The method is suitable for samples containing approximately 0.05 to 7.5% of silicon, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard silicon solution (1 ml = 75 µg of silicon). Transfer 0.0802 g of pure powdered silicon dioxide (dried at 150°C for 1 hour), and 0.4 g of high-purity silicon-free powdered ferric oxide (Fe_2O_3) to a 30-ml platinum crucible lined with 3 g of pre-melted anhydrous sodium tetraborate. Add 1 g of sodium tetraborate and mix thoroughly. Heat the mixture over an open flame for several minutes, then at approximately 1100°C for about 15 minutes or until a clear melt is obtained (Note 1). Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, and allow the crucible and contents to cool. Transfer the crucible and cover to a 400-ml Teflon beaker (Note 2), add 200 ml of 10% nitric acid, and heat gently, at approximately 90°C, until the dissolution of the melt is complete. Cool, remove the crucible and cover after washing them thoroughly with water, and transfer the resulting solution to a 500-ml volumetric flask. Dilute to volume with water, mix, and immediately transfer the solution to a polyethylene bottle. Dilute 20 ml of this stock solution to 100 ml with a blank solution, prepared in a similar manner and containing all of the reagents employed except the silicon dioxide (1 ml = 15 µg of silicon). Prepare fresh as required.

Ammonium molybdate solution, 12% w/v. Dissolve 120 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 500 ml of water, dilute to 1 litre, and transfer the solution to a polyethylene bottle. Allow the solution to stand for at least 1 day, filter it, if necessary, and store in a polyethylene bottle.

Oxalic acid solution, 5% w/v. Dissolve 50 g of oxalic acid dihydrate in approximately 800 ml of water, and dilute to 1 litre. Filter the solution, if necessary, and store in a polyethylene bottle.

Ascorbic acid solution, 2% w/v. Prepare fresh as required and store in a polyethylene bottle.

Nitric acid, 10% v/v. Store in a polyethylene bottle.

Sulphuric acid, 25% v/v. Store in a polyethylene bottle.

Hydrogen peroxide, 3% w/v. Dilute 10 ml of 30% hydrogen peroxide to 100 ml with water. Store in a polyethylene bottle.

Calibration curves

To four 100-ml volumetric flasks, add, by burette, 1, 2, 3, and 4 ml, respectively, of the dilute standard 15 µg/ml silicon solution, and to five additional flasks, add 1, 2, 3, 4, and 5 ml, respectively, of the 75 µg/ml solution. Dilute each solution to exactly 5 ml with the blank solution that was prepared by fusing 0.4 g of ferric oxide with 4 g of sodium tetraborate (Note 3). Add 5 ml of this solution to a tenth flask; this constitutes the blank. Add 2 ml of 10% nitric acid to each solution, then add 5 ml of 12% ammonium molybdate solution to the blank and the first two of the silicon solutions, and allow the solutions to stand for 5 minutes to complete the complex formation (Note 4). Add 10 ml of 5% oxalic acid solution, 5 ml of 25% sulphuric acid, and 5 ml of 2% ascorbic acid solution to each of the solutions, in rapid succession (Note 5), and mix thoroughly after each addition. Allow the solutions to stand for approximately 1 minute, and dilute to volume with water. Proceed, in a similar manner, with the formation and reduction of the β-silicomolybdic acid complex in the remaining solutions. Allow the solutions to stand for at least 5 minutes to complete the reduction, then determine the absorbance of each of the first four solutions, at 600 nm (Note 6), against the blank as the reference solution, using 5-cm cells. Determine the absorbance of each of the last five solutions in a similar manner, using 1-cm cells. Plot µg of silicon vs. absorbance for each series of measurements.

Procedure

In this procedure a reagent blank, prepared by fusing 0.4 g of ferric oxide with sodium tetraborate, is carried along with the samples (Note 7).

Decompose 0.5 g of powdered sample by fusion with 4 g of sodium tetraborate, using the decomposition technique described in the preparation of the standard silicon solution. After dissolution of the melt in 200 ml of 10% nitric acid (Note 8), transfer the resulting solution to a 500-ml volumetric flask. Dilute to volume with water, mix, and immediately transfer the solution to a polyethylene bottle.

Transfer 5-ml aliquots of both the sample and blank solutions (Note 9) to 100-ml volumetric flasks, add 2 ml of 10% nitric acid, and proceed with the formation and subsequent reduction of the silicomolybdic acid complex as described above. Measure the absorbance of the sample solution against the reagent blank solution, using 1- or 5-cm cells as required, and determine the silicon content of the aliquot by reference to the appropriate calibration curve.

Notes

1. This fusion technique facilitates decomposition, and inhibits attack on the platinum crucible by iron which results in the formation of an iron-platinum alloy. Complete decomposition of ferric oxide cannot readily be obtained by direct fusion with 4 g of sodium tetraborate.

2. Plasticware, previously cleaned with dilute hydrofluoric acid and washed with water, should be used whenever possible to avoid contamination by silica from glass. Glassware may be cleaned with 25% ammonium hydroxide and then washed with concentrated hydrochloric acid and water.

3. Iron is added to the solutions employed for the preparation of the calibration curve to counteract the slight effect of the iron, contained in iron ore, on the formation of the

silicomolybdic acid complex. The amount that is added is based on ores containing 56% of iron, but lesser or greater amounts may be present in the sample without producing significant error in the silicon result.

4. The β-silicomolybdic acid complex that is formed under these conditions is stable for approximately 30 minutes[5], then it slowly and irreversibly changes to the α-form[6].

5. Because oxalic acid quickly destroys the β-silicomolybdic acid complex[6-8], and the sulphuric acid hastens the transformation of the β-form to the α-form[6], these reagents, and the ascorbic acid solution, must be added, in rapid succession, to one solution at a time. The solution must be mixed thoroughly after each addition, and the neck of the flask should be washed down with the oxalic and sulphuric acid solutions, during the addition of these solutions, to prevent the subsequent reduction of any excess molybdate solution adhering to the walls of the flask.

6. Although the reduced β-silicomolybdic acid complex exhibits an intense absorption band at 810 nm, a less intense band or shoulder at approximately 600 nm is employed for spectrophotometric measurement to extend the effective upper range of the method. The lower range can be extended to approximately 0.005% of silicon if the absorbance (for up to approximately 25 μg of silicon) is measured at 810 nm using 5-cm cells.

7. The blank solution that is initially prepared for calibration purposes can be employed as the reagent blank if the same batch of reagents is used for fusion of the sample and for dissolution of the melt, and if the solution is relatively fresh and has been stored in a polyethylene container.

8. If the sample contains an appreciable amount of manganese, any manganese dioxide that may have precipitated during dissolution of the melt may be re-dissolved at this stage by the addition of several drops of 3% hydrogen peroxide. The solution must subsequently be boiled to eliminate excess hydrogen peroxide.

9. Samples containing more than 7.5% of silicon can be analyzed with reasonable accuracy by employing a smaller aliquot of the sample solution, diluted to 5 ml with the reagent blank solution, for complex formation.

Calculations

$$\%SiO_2 = 2.139 \times \%\ Si$$

References

1. Technical Committee 102 - Iron Ores, "Determination of the Silicon Content in Iron Ores", International Organization for Standardization, Document 193 E, December (1969).

2. A.B. Carlson and C.V. Banks, Anal. Chem., 24, 472 (1952).

3. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 2, pp 161-176 (1962).

4. M.C. Schwartz, Ind. Eng. Chem., Anal. Ed., 14, 893 (1942).

5. O.P. Case, ibid., 16, 309 (1944).

6. J.D.H. Strickland, J. Am. Chem. Soc., 74, 862, 868, 872 (1952).

7. M.A. DeSesa and L.B. Rogers, Anal. Chem., 26, 1278 (1954).

8. I.R. Morrison and A.L. Wilson, Analyst, 88, 88 (1963).

DETERMINATION OF SILICON IN FLUORSPAR BY THE SILICOMOLYBDIC ACID-NORMAL BUTYL ALCOHOL EXTRACTION METHOD

Principle

This method[1] is based on the formation of the yellow, heteropoly β-silico-12-molybdic acid complex in a dilute hydrochloric acid medium, and the subsequent extraction of the complex into normal butyl alcohol from a 1.8 M sulphuric acid medium. Silicon is determined by spectrophotometric measurement, at 400 nm, of the absorbance of the extract.

Outline

The sample is decomposed by fusion with sodium tetraborate to convert silica to the reactive monomeric form, and to prevent loss of silicon by volatilization as the tetrafluoride. The melt is dissolved in dilute hydrochloric acid. The resulting solution is analyzed for silicon.

Discussion of interferences

Phosphorus (V), arsenic (V), and germanium form similar yellow extractable heteropoly molybdate complexes under the conditions employed for the formation of the yellow β-silicomolybdic acid complex[2-4]. Germanium is not normally present in fluorspar, and interference from phosphorus and arsenic (up to at least 0.5 mg) is eliminated by adjusting the sulphuric acid concentration of the solution to approximately 1.8 M, and consequently destroying their complexes, prior to the extraction of the silicon complex[3-5].

Boric acid, which is formed during the dissolution of the sodium tetraborate melt, complexes and prevents interference from fluoride ion. The extraction procedure eliminates interference from coloured ions [copper (II), iron (III), and nickel]. Large amounts of calcium, magnesium, strontium, barium, alkali metals, nickel, copper, and zinc, and small amounts of iron, aluminum, tin, and manganese do not interfere[4-6].

Range

The method is suitable for samples containing approximately 0.05 to 5% of silicon, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard silicon solution (1 ml = 0.02 mg of silicon). Transfer 0.0107 g of pure powdered silicon dioxide (dried at 150°C for 1 hour), and 7 g of anhydrous sodium tetraborate to a 30-ml platinum crucible and mix thoroughly. Cover the crucible and carefully fuse the mixture over a blast burner for 3-5 minutes or until a clear melt is obtained. Transfer the cover, after allowing it to cool slightly, to a 400-ml polyethylene or Teflon beaker (Note 1) containing 150 ml of water and 25 ml of 50% hydrochloric acid. Remove the crucible from the source of heat, and carefully pour the hot melt into the beaker, by drops, so that most of the drops settle on top of the crucible cover (Note 2). When the crucible has cooled sufficiently, transfer it to the beaker, cover the beaker with a sheet of polyethylene, and secure the sheet to the beaker with a rubber band. Place the beaker in a steam-bath, and heat for approximately 2 hours or until the dissolution of the melt is complete (Note 3). Remove the crucible and cover after washing them thoroughly with water, cool the resulting solution to room temperature, and transfer it to a 250-ml volumetric flask. Dilute to volume with water, mix, and immediately transfer the solution to a polyethylene bottle. Prepare, in a similar manner, a blank solution containing all of the reagents employed above except the silicon dioxide.

Ammonium molybdate solution, 10% w/v. Dissolve 100 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 500 ml of water, dilute to 1 litre, and transfer the solution to a polyethylene bottle. Allow the solution to stand for at least 1 day, filter it, if necessary, and store in a polyethylene bottle.

Silica-free ammonia solution. Bubble ammonia gas into water, contained in a polyethylene bottle, until the solution is saturated (Note 4).

Hydrochloric acid, 50% v/v. Store in a polyethylene bottle.

Sulphuric acid, 50% and 1% v/v. Store in a polyethylene bottle.

Normal butyl alcohol. Analytical reagent-grade.

Calibration curve

To five 200-ml polyethylene beakers (Note 5), add, by burette, 10, 20, 30, 40, and 50 ml, respectively, of the standard 0.02 mg/ml silicon solution. By burette, dilute each solution to exactly 50 ml with the blank solution that was prepared by fusing 7 g of sodium tetraborate and dissolving the melt in dilute hydrochloric acid. Add 50 ml of this solution to a sixth beaker; this constitutes the blank. Using a pH meter, adjust the pH of each solution, if necessary, to 0.80 ± 0.05 with 50% hydrochloric acid or silica-free ammonia solution as required. Add 10 ml of 10% ammonium molybdate solution to each solution, mix thoroughly, and allow the solutions to stand for 10 minutes to complete the complex formation (Note 6).

Transfer the resulting solutions to 250-ml separatory funnels, marked at approximately 100 ml, and dilute to the mark with water. Add 25 ml of 50% sulphuric acid to the blank and the first of the silicon solutions, mix thoroughly, then, without delay (Note 7), add 75 ml of n-butyl alcohol, stopper, and shake for 1 minute. Proceed, in a similar manner, with the extraction of the β-silicomolybdic acid complex from the remaining solutions. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layers. Wash each alcohol layer 3 times by shaking for 30 seconds each time with a 20-ml portion of 1% sulphuric acid (Note 8). Drain off and discard the aqueous layers. Drain each butyl alcohol extract into a dry 100-ml volumetric flask, and wash the funnel twice with 5-ml portions of butyl alcohol. Add the washings to the flask, then add 1 ml of ethyl alcohol, dilute to volume with butyl alcohol and mix. Determine the absorbance of each extract, at 400 nm, against butyl alcohol as the reference solution, using 1-cm cells. Correct the absorbance value obtained for each β-silicomolybdic acid extract by subtracting that obtained for the blank extract. Plot mg of silicon vs. absorbance.

Procedure

In this procedure a reagent blank is carried along with the samples (Note 9).

Decompose 0.1-1 g of powdered sample, depending on the expected silicon content, by fusion with 7 g of sodium tetraborate as described above for the preparation of the standard silicon solution. After dissolution of the melt in dilute hydrochloric acid, transfer the resulting solution to a 250-ml volumetric flask. Dilute to volume with water, mix, and immediately transfer the solution to a polyethylene bottle.

Transfer 50-ml aliquots of both the sample and blank solutions (Note 10) to 200-ml polyethylene beakers, and proceed with the formation and extraction of the silicomolybdic acid complex, and the subsequent measurement of the absorbance as described above. Correct the absorbance value obtained for the sample extract by subtracting that obtained for the blank extract, and determine the silicon content of the aliquot by reference to the calibration curve.

Notes

1. Plastic beakers and bottles used for the dissolution of the melt and for storage of solutions, respectively, should be cleaned with dilute hydrofluoric acid and washed with water to prevent contamination from silica. Glassware may be cleaned with 25% ammonium hydroxide, and then washed with concentrated hydrochloric acid and water.

2. If polyethylene beakers are employed, the bottom of the beaker may melt if the hot melt is poured directly into the solution.

3. Occasional swirling of the solution during heating promotes dissolution of the melt.

4. The concentration of the solution can be tested periodically by titrating a 5-ml aliquot with concentrated hydrochloric acid, using phenolphthalein as indicator, and comparing the result obtained with that obtained from the titration of an identical portion of concentrated ammonium hydroxide.

5. Plastic beakers that have previously been employed for the formation of the silicomolybdic acid complex in samples containing phosphorus should be soaked for some time, preferably overnight, in 25% ammonium hydroxide, and then washed with concentrated hydrochloric acid and distilled water just before use. If this precaution is not taken, low results will be obtained for silicon, particularly with samples containing phosphorus[5], because of the "seeding effect" described by Morrison and Wilson[7], which results in precipitation of part of the phosphomolybdic acid.

6. The β-silicomolybdic acid complex that is formed under these conditions is stable for approximately 30 minutes, then it slowly and irreversibly changes to the α-form[8]. Consequently, if the ammonium molybdate solution is added to all of the solutions at the same time, the silicomolybdic acid complex in the resulting solutions must be extracted into butyl alcohol within a 20 minute time interval to avoid error (Note 7).

7. Because acidification of the solution hastens the transformation of β-silicomolybdic acid to the α-form[5,8], the sulphuric acid should be added to only one or two solutions at a time, and the subsequent extraction of the complex should be performed without delay. The complex is stable for at least 3 hours after extraction into an immiscible alcohol[5].

8. Washing the extract with dilute sulphuric acid partly removes co-extracted molybdic acid which absorbs at the wavelength employed for measurement of the absorbance of the silicon complex.

9. The blank solution prepared for calibration purposes can be employed as the reagent blank if the same batch of reagents is used for fusion of the sample and for dissolution of the melt, and if the solution is relatively fresh and has been stored in a polyethylene container.

10. Samples containing more than 5% of silicon can be analyzed with reasonable accuracy by employing a smaller aliquot of the sample solution, diluted to 50 ml with the reagent blank solution, for complex formation.

Calculations

$$\%SiO_2 = 2.139 \times \%Si$$

Other applications

By using appropriate acid-decomposition procedures this method can be employed to determine silicon in brass, bronze, and high-purity copper, magnesium, and nickel metals[5,6].

References

1. American Society for Testing and Materials, "Emission Spectroscopy; Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E 463-72, pp 1119-1121 (1973).

2. C. Wadelin and M.G. Mellon, Anal. Chem., 25, 1668 (1953).

3. E. Ruf, Z. Anal. Chem., 151, 169 (1956).

4. Idem, ibid., 161, 1 (1958).

5. Elsie M. Donaldson and W.R. Inman, "Determination of Silicon by Measurement of the Absorbance of the N-Amyl Alcohol Extract of α-Silicomolybdic Acid (Application to High-purity Copper Metal and Brasses)", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB 77, September (1965).

6. F.H. Harrison, Metallurgia, 66, 300 (1962).

7. I.R. Morrison and A.L. Wilson, Analyst, 88, 88 (1963).

8. J.D.H. Strickland, J. Am. Chem. Soc., 74, 862, 868, 872 (1952).

DETERMINATION OF TITANIUM IN ORES AND MILL PRODUCTS BY THE HYDROGEN PEROXIDE METHOD

Principle

Titanium is determined by spectrophotometric measurement, at 410 nm, of the absorbance of the yellow-orange titanium (IV)-hydrogen peroxide complex, formed in a 0.9 M sulphuric acid medium in the presence of phosphoric acid[1,2].

Outline

The sample is decomposed by fusion with potassium pyrosulphate. The melt is dissolved in dilute sulphuric acid, and insoluble material is removed by filtration. The resulting filtrate is analyzed for titanium.

Discussion of interferences

Interference from coloured ions [nickel, chromium (III), and uranium] is avoided by employing an identical aliquot of the sample solution, not treated with hydrogen peroxide, as the reference solution. Phosphoric acid eliminates interference from iron (III) by forming a colourless ferric phosphate complex.

Elements that form coloured complexes with hydrogen peroxide (vanadium, molybdenum, and niobium) and anions that form complexes with titanium (fluoride) interfere in this method[1,2].

> Note: For samples containing vanadium, and large amounts of molybdenum and tungsten the Spectrophotometric-Diantipyrylmethane Method for titanium (p 105) is recommended.

Range

The method is suitable for samples containing approximately 0.05 to 14% of titanium, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Reagents

Standard titanium solution (1 ml = 0.5 mg of titanium). Dissolve 0.4170 g of pure titanium dioxide by heating in a 300-ml Erlenmeyer flask with 10 g of ammonium sulphate and 20 ml of concentrated sulphuric acid. Cool and, using 5% sulphuric acid to wash the flask, transfer the resulting solution to a 500-ml volumetric flask containing approximately 400 ml of water. Dilute the solution to approximately 480 ml with 5% sulphuric acid, cool to room temperature, and dilute to volume with the same solution.

Hydrogen peroxide, 3% w/v. Dilute 10 ml of 30% hydrogen peroxide to 100 ml with water.

Sulphuric acid, 50% and 5% v/v.

Calibration curves

To eight 100-ml volumetric flasks, add, by burette, 0.5, 1, 1.5, 2, 4, 6, 10, and 14 ml, respectively, of the standard 0.5 mg/ml titanium solution, and dilute each solution to approximately 50 ml with 5% sulphuric acid. Add 50 ml of 5% sulphuric acid to a ninth flask; this constitutes the blank. Add 3 ml of concentrated phosphoric acid to each flask, mix thoroughly, then add 5 ml of 3% hydrogen peroxide, dilute the solutions to volume with 5% sulphuric acid and mix. Determine the absorbance of each of the first four titanium-hydrogen peroxide solutions, at 410 nm, against the blank as the reference solution, using 5-cm cells. Determine the absorbance of each of the last five solutions in a similar manner, using 1-cm cells. Plot mg of titanium vs. absorbance for each series of measurements.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.5 g of powdered sample to a 50-ml Vitreosil crucible, add approximately 10 g of potassium pyrosulphate, mix thoroughly, and cautiously (to avoid spattering) fuse the mixture over an open flame for 15-20 minutes. Cool, then transfer the crucible and contents to a 400-ml beaker containing approximately 100 ml of 5% sulphuric acid, and heat gently to dissolve the melt. Remove the crucible after washing it thoroughly with 5% sulphuric acid, and filter the solution (Whatman No. 30 paper) into a 250-ml volumetric flask, using 5% sulphuric acid to wash the beaker, paper, and residue (Note 1). Dilute the resulting solution to volume with 5% sulphuric acid and mix.

Transfer two identical 25-50-ml aliquots of both the blank and sample solutions to 100-ml volumetric flasks, dilute to approximately 50 ml with 5% sulphuric acid, if necessary, then, omitting the addition of hydrogen peroxide solution to one aliquot of each solution, proceed with the complex formation as described above. Measure the absorbance of the blank and sample solutions, using 1- or 5-cm cells as required, against the corresponding solutions, to which no hydrogen peroxide was added. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution, and determine the titanium content of the aliquot by reference to the appropriate calibration curve.

Notes

1. If the residue is suspected to contain titanium-bearing silicates, proceed as follows[3]:

Transfer the residue quantitatively to the filter paper, and transfer the paper and contents to a 30-ml platinum crucible. Burn off the paper at a low temperature, and ignite at approximately 600 C. Cool the crucible, and add 4 ml of 50% sulphuric acid and 3 ml each of concentrated nitric and hydrofluoric acids. Heat gently to decompose the residue, then evaporate the solution to dense fumes of sulphur trioxide. Cool, wash down the sides of the crucible with water and evaporate the solution to complete dryness. Fuse the residue with a small amount of potassium pyrosulphate, dissolve the melt, by heating gently, in approximately 15 ml of 5% sulphuric acid and, if necessary, filter the solution, using 5% sulphuric acid to wash the crucible and paper. Add the resulting solution to the initial filtrate, dilute the combined solution to volume with 5% sulphuric acid, mix, and proceed as described.

Calculations

$$\%TiO_2 = 1.668 \times \%\ Ti$$

Other applications

With modifications in the decomposition procedure and suitable separation of titanium from vanadium, molybdenum, and niobium, this method can be employed to determine titanium in iron, steel, and silicate rocks and minerals[1].

References

1. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 868-881 (1959).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 576-584 (1953).

3. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, 995 (1939).

DETERMINATION OF TITANIUM IN MOLYBDENUM AND TUNGSTEN ORES AND MILL PRODUCTS, IRON ORE, AND ACID-SOLUBLE SILICATE ROCKS AND MINERALS BY THE DIANTIPYRYLMETHANE METHOD

Principle

This method is based on that developed by Donaldson[1] and involves the formation of the yellow 1:3 titanium (IV)-diantipyrylmethane complex in a 1 M hydrochloric acid medium. Titanium is determined by spectrophotometric measurement, at 390 nm, of the absorbance of the complex. The molar absorptivity of the complex, at 390 nm, is 1.48×10^4 l. $\text{mole}^{-1}.\text{cm}^{-1}$.

Outline

Molybdenum and tungsten ores and mill products are decomposed with hydrochloric, nitric, hydrofluoric, and sulphuric acids, and the solution is evaporated to fumes of sulphur trioxide to remove silica and excess hydrofluoric acid. The acid-insoluble material is ultimately removed by filtration, ignited, and fused with potassium pyrosulphate. The melt is dissolved in dilute sulphuric acid, and the resultant solution is added to the initial filtrate. Titanium is subsequently separated from molybdenum and tungsten by chloroform extraction of its cupferron complex from an alkaline ammonium tartrate-ethylenediaminetetra-acetic acid (EDTA)-sodium sulphite medium. The chloroform extract is evaporated to dryness, and the salts are ultimately dissolved in dilute sulphuric acid. The resulting solution is analyzed for titanium.

Iron ores and silicate rocks and minerals are decomposed as described above, and the solution is ultimately diluted with dilute sulphuric acid. Iron, if present in large amounts, is removed by a mercury cathode separation. The resulting solution, or the preceding solution, if large amounts of iron are absent, is ultimately analyzed for titanium.

Discussion of interferences

Coloured ions [chromium (III), chromium (VI), copper, cobalt, nickel, and molybdenum], elements that cannot be maintained in solution during complex formation (tungsten, in large amounts), and ions that form coloured complexes with diantipyrylmethane in 1 M hydrochloric acid media [iron (III) and vanadium (V)] interfere in the determination of titanium with diantipyrylmethane. Interference from all of the above elements, except iron, is avoided in the method for molybdenum and tungsten ores and mill products by separating titanium from these elements, and from various other elements (e.g., zinc, cadmium, bismuth, and phosphate ion) by chloroform extraction of its cupferron complex from an ammoniacal (pH 8) medium, in the presence of ammonium tartrate and EDTA as complexing agents[1]. During the extraction procedure, interference from manganese, which is air-oxidized to the trivalent state in alkaline media and subsequently causes incomplete extraction of titanium [presumably because of its catalytic reduction to titanium (III)], is eliminated with sodium sulphite. Iron is partly co-extracted as its cupferron complex under the conditions employed for the separation of titanium, but interference from iron (III) is eliminated by reducing it to the divalent state with ascorbic acid prior to complex formation. Up to 20 mg of iron, and at least 5 mg of other elements that are partly co-extracted [i.e., zirconium, thorium, tin (IV), aluminum, and antimony (III)] can be present in the solution or aliquot taken for analysis without affecting the titanium result[1].

In the method for iron ores and silicate rocks and minerals, interference from more than 20 mg of iron and from coloured ions is avoided by removing these ions by a mercury cathode separation. Up to approximately 1 mg of vanadium, copper, cobalt, nickel, and molybdenum do not cause significant error in the titanium result.

Range

The method is suitable for molybdenum and tungsten ores and mill products containing approximately 0.01 to 5% of titanium, and for iron ores and silicate rocks and minerals containing approximately 0.005 to 6% of titanium.

Apparatus

Mercury cathode.

Reagents

Standard titanium solution (1 ml = 0.2 mg of titanium). Dissolve 0.1668 g of pure titanium dioxide by heating in a 125-ml Erlenmeyer flask with 8 g of ammonium sulphate and 25 ml of concentrated sulphuric acid. Cool and, using 5% sulphuric acid to wash the flask, transfer the resulting solution to a 500-ml volumetric flask containing approximately 350 ml of water. Dilute the solution to approximately 480 ml with 5% sulphuric acid, cool to room temperature, and dilute to volume with the same solution. Dilute 10 ml of this stock solution to 200 ml with 5% sulphuric acid (1 ml = 10 µg of titanium). Prepare fresh as required.

Diantipyrylmethane solution, 3% w/v in 1 M hydrochloric acid. Dissolve 6 g of 4, 4-methylenediantipyrine in 50 ml of water containing 17 ml of concentrated hydrochloric acid. Add 10 ml of 10% ascorbic acid solution, filter the solution, and dilute to 200 ml with water. Prepare a fresh solution every 2 days.

Ascorbic acid solution, 10% w/v. Prepare a fresh solution every 2 days.

Ethylenediaminetetra-acetic acid (EDTA), disodium salt solution, 10% w/v. Dissolve 20 g of the reagent in approximately 150 ml of hot water, cool, and dilute to 200 ml.

Ammonium tartrate solution, 25% w/v.

Hydrochloric acid, 9 M. Dilute 385 ml of concentrated acid to 500 ml with water.

Cupferron solution, 5% w/v. Prepare fresh as required.

Sodium sulphite solution, 10% w/v. Prepare fresh as required.

Sulphuric acid, 50% and 5% v/v.

Sodium hydroxide solutions, 50% and 25% w/v.

Hydrochloric acid, 25% v/v.

Chloroform. Analytical reagent-grade.

Calibration curve

Add 5 ml of 50% sulphuric acid to each of six 100-ml beakers; then, by burette, add to the last five beakers 1, 2, 3, 5, and 7.5 ml, respectively, of the dilute standard 10 µg/ml titanium solution. The contents of the first beaker constitute the blank. Add 2 ml of 25% ammonium tartrate solution and 5 ml of 10% ascorbic acid solution to each beaker and, using a pH meter, adjust the pH of the resulting solution to 6.5 ± 0.5 (Note 1) with concentrated ammonium hydroxide. Add 10 ml of 9 M hydrochloric acid, transfer the solution to a 100-ml volumetric flask, and cool to room temperature. Add 10 ml of 3% diantipyrylmethane solution, dilute to volume with water, mix, and allow the solution to stand for at least 30 minutes to complete the complex formation (Note 2). Determine the absorbance of each solution, at 390 nm, against the blank as the reference solution, using 4-cm cells. Plot µg of titanium vs. absorbance.

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Molybdenum and tungsten ores and mill products

Transfer 0.25-0.5 g of powdered sample, depending on the expected titanium content, to a 250-ml Teflon beaker, and add 15 ml of 50% sulphuric acid and 5 ml each of concentrated hydrochloric, nitric, and hydrofluoric acids. Cover the beaker with a Teflon cover, and heat gently until the decomposition of silicates and acid-soluble material is complete, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with 5% sulphuric acid, and again evaporate the solution to fumes to ensure the complete removal of hydrofluoric acid. Cool, add 40 ml of 5% sulphuric acid, and heat gently to dissolve the soluble salts (Note 3). Filter the resulting solution (Whatman No. 40 paper) into a 250-ml volumetric flask, using 5% sulphuric acid to wash the beaker, paper, and residue, and transfer the residue quantitatively to the filter paper.

Transfer the paper and contents to a 30-ml Vitreosil crucible, burn off the paper at a low temperature, and ignite at approximately 600°C. Fuse the residue with 2 g of potassium pyrosulphate, cool, and transfer the crucible and contents to a 250-ml beaker. Add 50 ml of 5% sulphuric acid and 10 ml of 25% ammonium tartrate solution, boil to dissolve the melt, and remove the crucible after washing it thoroughly with 5% sulphuric acid ((Note 4). If necessary, filter the resulting solution (Whatman No. 42 paper) into the flask containing the initial filtrate, using 5% sulphuric acid to wash the beaker and paper. Cool the combined solution to room temperature, dilute to volume with 5% sulphuric acid and mix.

Transfer a 10-25-ml aliquot, containing up to approximately 0.5 mg of titanium (Note 5), to a 250-ml beaker, and dilute to approximately 25 ml with 5% sulphuric acid. Add, in succession, sufficient 25% ammonium tartrate solution so that approximately 5 ml are present, 5 ml of 10% EDTA solution, 10 ml of 10% sodium sulphite solution, and a small piece of red litmus paper, and neutralize the resulting solution approximately with 50% sodium hydroxide solution. Allow the solution to cool to room temperature, then, using a pH meter, adjust the pH to 8.0 ± 0.1 with 25% sodium hydroxide solution and/or 25% hydrochloric acid as required. Transfer the solution to a 125-ml separatory funnel, and add 10 ml of 5% cupferron solution (Note 6). Mix the solution, add 5 ml of chloroform, stopper, and shake for 2 minutes. Allow several minutes for the layers to separate, then drain the chloroform extract into a 100-ml beaker. Re-extract the sample solution three more times, using 5 ml of chloroform, and shaking for 2 minutes each time (Note 7). Combine these extracts with the first one, and evaporate the combined extracts to dryness in a hot water-bath. Add 5 ml each of 50% sulphuric acid, water, and concentrated hydrochloric and nitric acids to the resulting residue. Cover the beaker and boil the solution to destroy organic material, then remove the cover and evaporate the solution to fumes of sulphur trioxide (Note 8). Cool, wash down the sides of the beaker with a small amount of 5% sulphuric acid and again evaporate the solution to fumes (Note 8).

If the aliquot taken for analysis contains 75 µg or less of titanium, dilute both the sample and blank solutions by adding approximately 5 ml of 5% sulphuric acid and, omitting the addition of 5 ml of 50% sulphuric acid, proceed (Note 9) with the formation of the titanium-diantipyrylmethane complex as described above. Measure the absorbance of the sample solution against the reagent blank solution, and determine the titanium content of the aliquot by reference to the calibration curve.

If the aliquot contains more than 75 µg of titanium, dilute both the sample and blank solutions by adding approximately 10 ml of 5% sulphuric acid. If necessary, filter the solutions (Whatman No. 40 paper) into 50-ml volumetric flasks, using 5% sulphuric acid to wash the beaker and paper, dilute to volume with the same solution and mix. Transfer a 5- or 10-ml aliquot of both solutions to 100-ml beakers, add sufficient 50% sulphuric acid (i.e., 4 or 3 ml, respectively) so that approximately 2.5 ml of concentrated acid are present (Note 10), and proceed with the complex formation and subsequent determination of titanium as described above.

B - Iron ore and acid-soluble silicate rocks and minerals

(a) Titanium content 0.03% or less

Decompose 0.5 g of powdered sample by the method described in Procedure A , using 10 ml of 50% sulphuric acid rather than 15 ml and, if necessary, repeat the addition of hydrofluoric, hydrochloric, and nitric acids until the decomposition of the sample is complete. Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes of sulphur trioxide. Repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid, then add 40 ml of 5% sulphuric acid and heat gently to dissolve the salts. If necessary (Note 11), filter the solution (Whatman No. 42 paper) into a 500-ml volumetric flask, using 5% sulphuric acid to wash the beaker and paper, dilute to volume with the same solution and mix.

Transfer a 100-ml aliquot of the resulting solution to a mercury cathode cell, and electrolyze the solution for 1 hour at approximately 10 amperes. Filter the electrolyte (Whatman No. 40 paper) into a 250-ml beaker, using 5% sulphuric acid to wash the cathode cell and paper. Add 5 ml of concentrated hydrochloric acid to volatilize any residual mercury salts present, and evaporate the solution until approximately 2.5 ml of sulphuric acid remain (Note 8). Dilute both the sample and blank solutions by adding approximately 5 ml of 5% sulphuric acid, then proceed with the complex formation and subsequent determination of titanium as described above.

(b) Titanium content greater than 0.03%

Decompose 0.25-0.5 g of sample, depending on the expected titanium content, by the method described above. After evaporation of the resulting solution to fumes of sulphur trioxide three times, and dissolution of the salts in 40 ml of 5% sulphuric acid, filter the solution (Whatman No. 42 paper), if necessary (Note 11), into a volumetric flask of appropriate size (250-1000 ml), using 5% sulphuric acid to wash the beaker and paper. Dilute the solution to volume with the same solution and mix (Note 12).

Transfer a 5- or 10-ml aliquot of both the sample and blank solutions to 100-ml beakers, add sufficient 50% sulphuric acid so that approximately 2.5 ml of concentrated acid are present, and determine the titanium content of the aliquot as described above.

Notes

1. This pH adjustment is adequate even though the solution becomes hot at this stage.

2. The titanium-diantipyrylmethane complex that is formed under these conditions is stable for at least 3 days[1].

3. Tungsten, if present, is in the insoluble yellow hydrated trioxide form at this stage, and will constitute part of the acid-insoluble residue after filtration.

4. If the sample contains an appreciable amount of tungsten, the solution of the melt may be cloudy, or may contain a white precipitate. If this occurs, add sufficient 50% sodium hydroxide solution to clarify the solution, then, using litmus paper, neutralize the resulting solution approximately with 50% sulphuric acid, add 10 ml in excess and proceed as described.

5. Up to at least 0.5 mg of titanium can be separated from large amounts of molybdenum and tungsten, and various other elements by the subsequent cupferron-chloroform extraction step[1]. Larger amounts can probably be extracted if more cupferron is employed, and if the number of extraction stages is increased.

6. The distinctive yellow titanium-cupferron complex, which precipitates in acid media, does not precipitate, and cannot be observed visually in alkaline media[1].

7. Additional cupferron solution is not required in the subsequent extraction stages, because the excess cupferron, contrary to extraction from acid media, is not extracted from alkaline media[1].

8. Care should be taken that the solution is evaporated just to fumes of sulphur trioxide. If the whole solution is taken for analysis, approximately 2.5 ml of concentrated sulphuric acid should be present prior to complex formation (Note 10). Sulphuric acid, or other acid solutions of titanium should not be evaporated to dryness or near dryness. This can cause low results for titanium because the deposited salts are not readily re-dissolved[2].

9. If the solution is not completely clear after adjustment to pH 6.5 ± 0.5 and acidification with 9 M hydrochloric acid, it may be clarified by filtration prior to the addition of diantipyrylmethane solution.

10. If the solution or aliquot contains less than approximately 2.5 ml of concentrated sulphuric acid, slightly low results will be obtained for titanium, presumably due to partial hydrolysis of titanium during the pH adjustment step[1].

11. Silicate rock and mineral solutions may contain some insoluble calcium sulphate at this stage; this can be removed by filtration and discarded. If some acid-insoluble residue is present in iron ore solutions, proceed as follows:

Transfer the residue quantitatively to the filter paper, then transfer the paper and contents to a 30-ml platinum crucible and ignite and fuse the residue as described in Procedure A. Dissolve the melt in 50 ml of 5% sulphuric acid and add the resulting solution to the initial filtrate. Dilute the combined solution to volume with 5% sulphuric acid, mix, and proceed as described.

12. If the sample contains an appreciable amount of chromium and/or other coloured ions, these can be separated from titanium at this stage by the mercury cathode separation described in the previous procedure. If this separation technique is employed, evaporate the electrolyte as described, dilute the final solution to 100 ml with 5% sulphuric acid, and proceed with the determination of titanium as described.

Calculations

$$\%TiO_2 = 1.668 \times \%\ Ti$$

Other applications

With modifications in the decomposition procedure, this method can be employed to determine titanium in aluminum metal, after separation of titanium by chloroform extraction of its cupferron complex from an approximately 10% sulphuric acid medium; in aluminum-base alloys, after removal of various interfering elements by a mercury cathode separation, followed by separation of titanium from aluminum as described above; and in cast iron, steel, and nickel-base alloys, after removal of the matrix elements by a mercury cathode separation.

References

1. Elsie M. Donaldson, Talanta, 16, 1505 (1969).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 577 (1953).

DETERMINATION OF TUNGSTEN IN ORES AND MILL PRODUCTS BY THE THIOCYANATE METHOD

Principle

This method[1] is a modification of that developed by Freund et al[2], and is based on the formation of the yellow tungsten-thiocyanate complex after reduction of tungsten with stannous chloride in an approximately 1.8 M sulphuric-2.3 M hydrochloric acid medium. Tungsten is determined either by direct spectrophotometric measurement, at 400 nm, of the absorbance of the complex in the aqueous medium, or after extraction of the complex into isopropyl ether.

Outline

Low-grade ores and mill products containing tungsten minerals other than wolframite (e.g., scheelite, ferberite, and hübnerite) are decomposed with hydrochloric, hydrofluoric, and phosphoric acids. The solution is evaporated to a paste to remove excess hydrofluoric acid, and the paste is dissolved in dilute hydrochloric acid. If both iron and molybdenum are present, iron is separated from molybdenum and tungsten by isopropyl ether extraction of its chloro complex. The resulting aqueous phase, or the preceding solution, if both iron and molybdenum are absent, is ultimately analyzed for tungsten.

High-grade ores and mill products and those containing wolframite are decomposed by fusion with potassium pyrosulphate, and the melt is dissolved in dilute tartaric acid solution. The resulting solution is analyzed for tungsten.

Discussion of interferences

The extraction procedure eliminates interference from coloured ions (chromium, nickel, cobalt, and vanadium), and from ions that form coloured thiocyanate complexes (uranium, titanium and niobium) under the conditions employed for the formation of the tungsten complex[1]. It also increases the sensitivity of the method for the determination of small amounts of tungsten.

Moderate amounts of aluminum, antimony, bismuth, lead, manganese, zirconium, and iron, and large amounts of tartrate, phosphate, and borate do not interfere[1,3]. Arsenic, selenium and tellurium are reduced to the elemental state with stannous chloride, but these elements do not interfere when tungsten is determined after extraction of the complex into isopropyl ether. Copper, in large amounts, interferes by precipitating as cuprous thiocyanate[3]. Molybdenum, when present in conjunction with iron, produces high results for tungsten, but this interference is essentially eliminated by separating the iron by isopropyl ether extraction of its chloro complex from a hydrochloric acid medium. Up to 20 mg of molybdenum alone can be present in the aliquot taken for analysis without producing appreciable error in the tungsten result[1].

Range

The method is suitable for low-grade ore and mill product samples containing more than approximately 0.005% of tungsten. High-grade samples containing up to approximately 50% of tungsten can be analyzed with reasonable accuracy.

Reagents

Standard tungsten solution (1 ml = 1 mg of tungsten). Dissolve 0.8973 g of sodium tungstate ($Na_2WO_4.2H_2O$) in water and dilute to 500 ml. Dilute 20 ml of this stock solution to 200 ml with water (1 ml = 0.1 mg of tungsten).

Potassium thiocyanate solution, 20% w/v. Prepare a fresh solution daily.

Stannous chloride solution, 45% w/v. Dissolve 113 g of stannous chloride dihydrate in concentrated hydrochloric acid and dilute to 250 ml with the same acid.

Tartaric acid solution, 7.5% w/v.

Hydrochloric acid, 20% v/v.

Sulphuric-hydrochloric acid solution, 10% and 20% v/v, respectively.

Hydrochloric acid, 8 M. Dilute 340 ml of concentrated acid to 500 ml with water.

Isopropyl ether (peroxide-free).

Calibration curves

Aqueous medium

To six 100-ml volumetric flasks, add, by burette, 1, 2.5, 5, 7.5, 10, and 15 ml, respectively, of the dilute standard 0.1 mg/ml tungsten solution, and dilute each solution to approximately 15 ml with water. Add 15 ml of water to a seventh flask; this constitutes the blank. Add 10 ml of concentrated sulphuric acid, 20 ml of concentrated hydrochloric acid, and 5 ml of 45% stannous chloride solution to each flask, mix thoroughly after each addition, then place the flask in a boiling water-bath for 1 hour (Note 1). Remove the flask, add 10 ml of water, mix, and cool the resulting solution to approximately 10-15°C in an ice-bath. Add 10 ml of 20% potassium thiocyanate solution, dilute to volume with water, mix, and allow the solution to stand at room temperature for 10 minutes. Determine the absorbance of each solution, at 400 nm, against water as the reference solution, using 1-cm cells. Correct the absorbance value obtained for each tungsten-thiocyanate solution by subtracting that obtained for the blank solution. Plot mg of tungsten vs. absorbance.

Isopropyl ether medium

Transfer 10-ml aliquots of the first five of the above solutions (containing 10, 25, 50, 75, and 100 µg of tungsten) and the blank solution to 125-ml separatory funnels marked at approximately 50 ml. Dilute to the mark with 10% sulphuric-20% hydrochloric acid solution and mix. By pipette, add 10 ml of peroxide-free isopropyl ether to each funnel, stopper, and shake for 30 seconds. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layer. Determine the absorbance of each extract as described above, using isopropyl ether as the reference solution. Correct the absorbance value obtained for each tungsten-thiocyanate extract by subtracting that obtained for the blank extract. Plot µg of tungsten vs. absorbance.

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Low-grade ores and mill products

(a) Either iron or molybdenum present

Transfer 0.1-2 g of powdered sample, depending on the expected tungsten content, to a 100-ml platinum dish, and add 15 ml each of concentrated hydrochloric and hydrofluoric acids. Heat gently for approximately 30 minutes to decompose siliceous materials, then add 1 ml of concentrated phosphoric acid, and allow the mixture to digest on a hot-plate until it has evaporated to a paste. Cool, add 10 ml of 20% hydrochloric acid and stir until the paste has dissolved. If necessary (Note 2), filter the resulting solution (Whatman No. 540 paper) into a volumetric flask of appropriate size (100 or 200 ml), dilute to volume with water and mix. Transfer a 5- or 10-ml aliquot of both the sample and blank solutions to 100-ml volumetric flasks, dilute to approximately 15 ml with water, and proceed with the reduction and subsequent formation of the tungsten-thiocyanate complex as described above.

In the absence of coloured ions, and ions that form coloured thiocyanate complexes, measure the absorbance of the sample and blank solutions as described under "Aqueous medium". Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution, and determine the tungsten content of the aliquot by reference to the calibration curve.

If coloured ions or other coloured thiocyanate complexes are present (Note 3), or if the tungsten content of the aliquot is less than 0.05 mg, transfer suitable aliquots (up to 50 ml) of both the sample and blank solutions to 125-ml separatory funnels. Dilute to 50 ml with 10% sulphuric-20% hydrochloric acid solution, if necessary, and proceed with the extraction of the tungsten-thiocyanate complex and the subsequent measurement of the absorbance as described under "Isopropyl ether medium". Correct the absorbance value obtained for the sample extract by subtracting that obtained for the blank extract, and determine the tungsten content of the aliquot by reference to the calibration curve.

(b) Both iron and molybdenum present

Following sample decomposition and evaporation of the resulting mixture to a paste as described above, add 20 ml of 8 M hydrochloric acid and stir until the paste has dissolved. Transfer the solution to a 60-ml separatory funnel marked at approximately 30 ml, using a small amount of 8 M hydrochloric acid to wash the platinum dish, and dilute to the mark with the same solution. Add 15 ml of peroxide-free isopropyl ether, stopper, and shake for 1-2 minutes. Allow several minutes for the layers to separate, then drain the lower aqueous layer into a second 60-ml separatory funnel and re-extract the solution with 15 ml of isopropyl ether. Repeat the extraction one more time, allow the layers to separate, then drain the aqueous layer into a 250-ml beaker. Wash each ether layer twice by shaking for 30 seconds each time with 2-3-ml portions of 8 M hydrochloric acid, and add the washings to the beaker containing the aqueous phase. Heat the combined solution gently to remove the residual ether, cool to room temperature, and transfer the solution to a volumetric flask of appropriate size (100 or 200 ml). Dilute the solution to volume with water, mix, and determine the tungsten content of a suitable aliquot as described above.

B - High-grade ores and mill products and those containing wolframite

Transfer 0.1-0.5 g of powdered sample, depending on the expected tungsten content, to a 50-ml Vitreosil crucible, add 4-5 g of potassium pyrosulphate and mix thoroughly. Cover the mixture with approximately 0.5 g of potassium pyrosulphate, and fuse it over an open flame for about 5 minutes. Cool, transfer the crucible and contents to a 400-ml beaker, and add 100-150 ml of 7.5% tartaric acid solution. Heat gently to dissolve the melt, then remove the crucible after washing it thoroughly with 7.5% tartaric acid solution. Filter the resulting solution (Whatman No. 540 paper) into a volumetric flask of appropriate size (200-500 ml), using 7.5% tartaric acid solution to wash the beaker and paper. Dilute the solution to volume with the same solution, mix, and determine the tungsten content of a suitable aliquot as described in Procedure A (a) (Note 4).

Notes

1. A reduction period of 1 hour in a boiling water-bath is recommended; shorter reduction periods may yield low and erratic results for tungsten. Direct boiling on a hot-plate also causes low results[1].

2. Any acid-insoluble material remaining at this stage may be ignited and fused with a small amount of potassium pyrosulphate, followed by dissolution of the melt in 7.5% tartaric acid solution, and addition of the resulting solution to the initial filtrate (Note 4).

3. The presence of iron is indicated in samples containing molybdenum if the extract is orange instead of greenish-yellow. If this is observed, the sample should be analyzed by Procedure A (b).

4. The extraction of the tungsten-thiocyanate complex into isopropyl ether is not applicable after sample decomposition by fusion. Emulsification occurs in the ether layer during the extraction step because of the presence of large amounts of potassium salts and tartaric acid[1].

Calculations

$$\%WO_3 = 1.261 \times \%\ W$$

Other applications

With modifications in the decomposition procedure this method can be employed to determine tungsten in steel and silicate rocks and minerals[1].

References

1. G.H. Faye, R.J. Guest and R.C. McAdam, "The Determination of Tungsten in Ores, Concentrates, and Steels", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Technical Bulletin TB 37, May (1962).

2. H. Freund, M.L. Wright and R.K. Brookshier, Anal. Chem., 23, 781 (1951).

3. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 886-889 (1959).

DETERMINATION OF VANADIUM IN ACID-SOLUBLE SILICATE ROCKS AND MINERALS, SILICA SAND, SANDSTONE, QUARTZITE, CARBONATE ROCKS, CLAY, AND SHALE BY THE N-BENZOYL-N-PHENYLHYDROXYLAMINE METHOD

Principle

Vanadium is determined by spectrophotometric measurement, at 475 nm, of the absorbance of a red vanadium (V)-N-benzoyl-N-phenylhydroxylamine (NBPHA) complex, which is extracted into chloroform from a 2 M sulphuric-4 M hydrofluoric acid medium containing ammonium persulphate as oxidant[1]. The molar absorptivity of the complex, at 475 nm, is 4.28×10^3 l. mole^{-1}. cm^{-1}.

Outline

The sample is decomposed with hydrofluoric, nitric, and sulphuric acids. The solution is evaporated to fumes of sulphur trioxide to remove silica and excess nitric acid, and the salts are dissolved in water. The resulting solution is ultimately analyzed for vanadium.

Discussion of interferences

Common ions [magnesium, calcium, aluminum, manganese (II), cobalt, nickel, copper (II), cadmium, zinc, bismuth, arsenic (V), antimony (III), antimony (V), and tin (IV)]; up to at least 500 mg of iron, niobium, tantalum, titanium, and zirconium; and up to 50 mg of molybdenum and tungsten do not interfere in this method. Chromium and cerium interfere if they are present in the hexavalent and tetravalent states, respectively. Interference from moderate amounts of these elements (up to approximately 10 mg) is eliminated by reducing these ions to the trivalent state with iron (II). Vanadium is also reduced by iron (II) but is subsequently re-oxidized to the pentavalent state with ammonium persulphate; chromium (III) and cerium (III) are not re-oxidized under these conditions, except possibly when silver is present[1].

Range

The method is suitable for samples containing approximately 0.0005 to 0.15% of vanadium, but material containing higher concentrations can also be analyzed if a smaller sample or a suitable aliquot of a sulphuric acid solution of the sample is taken.

Apparatus

Polypropylene separatory funnels. 125-ml pear-shape type.

Reagents

Standard vanadium solution (1 ml = 0.2 mg of vanadium). Dissolve 0.1785 g of pure vanadium pentoxide (Note 1) by heating with 40 ml of 12.5 M sulphuric acid and 5 ml of concentrated nitric acid. Evaporate the resulting solution to fumes of sulphur trioxide, cool, and dilute to 500 ml with water. Dilute 25 ml of this stock solution to 200 ml with water. Prepare fresh as required (1 ml = 25 μg of vanadium).

NBPHA solution, 0.1% w/v in chloroform. Store in a brown bottle.

Ferrous ammonium sulphate solution, 10% w/v. Dissolve 5 g of ferrous ammonium sulphate hexahydrate in approximately 30 ml of water, add 1 ml of 12.5 M sulphuric acid and dilute the solution to 50 ml with water. Prepare fresh as required.

Ammonium persulphate solution, 10% w/v. Prepare fresh as required.

Sulphuric acid, 12.5 M. Add 695 ml of concentrated sulphuric acid, slowly and while stirring, to 275 ml of water in a 1500-ml pyrex beaker. Allow the solution to cool to room temperature, transfer it to a 1-litre volumetric flask, and dilute to volume with water.

Hydrofluoric acid, 25 M. Dilute 218 ml of concentrated hydrofluoric acid to 250 ml with water in a polyethylene bottle.

Chloroform (alcohol-free). Chromatoquality-reagent. Reagent-grade chloroform can be purified by washing it 5 or 6 times with water, followed by distillation, after drying over calcium chloride[2].

Calibration curve

Add 8 ml of 12.5 M sulphuric acid to each of seven 125-ml polypropylene separatory funnels marked at approximately 50 ml; then, by burette, add to the last six funnels 1, 2, 3, 4, 5, and 6 ml, respectively, of the dilute standard 25 µg/ml vanadium solution. The contents of the first funnel constitute the blank. Add 8 ml of 25 M hydrofluoric acid and 4 ml of 10% ferrous ammonium sulphate solution to each funnel, in succession, dilute the solutions to approximately 40 ml with water and mix. Add 5 ml of 10% ammonium persulphate solution, dilute to the 50-ml mark with water and mix thoroughly. Add 10 ml of 0.1% NBPHA-chloroform solution, stopper, and shake for 2 minutes. Allow several minutes for the layers to separate, then filter the chloroform extract through a wad of cotton-wool into a dry 25-ml volumetric flask. Re-extract the solution three more times using, in succession, 5, 3, and 3 ml of NBPHA solution and shaking for 2 minutes each time. Combine these extracts with the first, then wash the funnel and cotton-wool with a few ml of chloroform, and dilute to volume with chloroform (Note 2). Determine the absorbance of each solution, at 475 nm, against chloroform as the reference solution, using 2-cm cells. Correct the absorbance value obtained for each vanadium-NBPHA solution by subtracting that obtained for the blank solution. Plot µg of vanadium vs. absorbance.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.1-0.5 g of powdered sample, depending on the expected vanadium content, to a 250-ml Teflon beaker. Add 8 ml of 12.5 M sulphuric acid and 5 ml each of water and concentrated hydrofluoric and nitric acids, and allow the mixture to digest at room temperature for approximately 30 minutes. Evaporate the resulting solution to fumes of sulphur trioxide, cool and, if necessary, repeat the addition of water and concentrated hydrofluoric and nitric acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the beaker with a small amount of water, and again evaporate the solution to fumes to ensure the complete removal of nitric acid. Cool, add 5 ml of water and, if necessary, heat gently to clarify the solution. Allow the solution to cool to room temperature (Note 3), then, just before the extraction step, add 8 ml of 25 M hydrofluoric acid (Notes 4 and 5). Transfer the resulting solution to a 125-ml polypropylene separatory funnel, and proceed with the extraction of vanadium and the subsequent measurement of the absorbance as described above. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution and determine the vanadium content of the sample solution by reference to the calibration curve.

Notes

1. If the purity of the vanadium pentoxide is in doubt, the vanadium content of the reagent can be determined as follows[3], and the standard solution can be prepared accordingly:

Transfer 0.2000 g of the vanadium pentoxide to a 250-ml beaker, add approximately 10 ml of water and 3 ml of concentrated sulphuric acid (or 4 ml of 12.5 M sulphuric acid), and heat until the oxide has dissolved. Dilute the solution to approximately 125 ml with water, add 1 g of sodium sulphite, in small portions, to reduce the vanadium to the tetravalent state, and boil the solution (un-covered) for 15-20 minutes to expel the excess sulphur dioxide. Titrate the hot solution with standard 0.1 N potassium permanganate solution (1 ml = 5.094 mg of vanadium), previously standardized against sodium oxalate as described in the Volumetric-Oxalate Method for calcium (p 242), until the colour of the solution just changes from a pure yellow. Correct the result obtained by subtracting that obtained for a blank that is carried through the same procedure.

Then,

$$\%V = \frac{(V - v) \times N \times 50.94}{\text{Weight of } V_2O_5 \text{taken (mg)}} \times 100$$

where:

V = *volume (ml) of potassium permanganate solution required by the vanadium pentoxide,*

v = *volume (ml) of potassium permanganate solution required by the blank,*

N = *normality of the potassium permanganate solution,*

and the weight (g) of vanadium pentoxide required for the standard solution

$$= 0.1785 \times \frac{56.01}{\text{Vanadium found (\%)}}$$

where:

56.01 = *the theoretical percentage of vanadium in pure vanadium pentoxide.*

If vanadium pentoxide is not available, ammonium metavanadate (NH_4VO_3) can be employed for the preparation of the standard vanadium solution, but the purity of the reagent should be checked as described above.

2. The absorbance of the chloroform solution of the vanadium-NBPHA complex remains constant for at least 24 hours[1].

3. Samples containing more than 0.15% of vanadium can be analyzed at this stage if the solution is diluted to volume with water in a volumetric flask of appropriate size, and a suitable aliquot (up to 20 ml) of the resulting solution is taken. If this method is employed, sufficient 12.5 M sulphuric acid must be added to the aliquot in the separatory funnel so that the sulphuric acid concentration of the final solution will be 2 M when the solution is diluted to 50 ml prior to the extraction of vanadium.

4. The hydrofluoric acid must be added just before the extraction step because it volatilizes from the solution on prolonged standing at room temperature[1].

5. Any insoluble calcium sulphate that may be present at this stage does not interfere with the extraction of vanadium.

Calculations

$$\%V_2O_5 = 1.785 \times \% V$$

$$\%V_2O_3 = 1.471 \times \% V$$

Other applications

With modifications in the decomposition and sample preparation procedures (e.g., a mercury cathode separation where applicable) prior to extraction, this method can be employed to determine vanadium in steel, cast iron, nonferrous alloys, cobalt and nickel arsenides, niobium, tantalum, molybdenum, tungsten, titanium, and zirconium metals. It should be applicable to refractory silicate rocks and minerals, and molybdenum and tungsten ores after sample decomposition by fusion with sodium carbonate, followed by removal of silica by volatilization from a sulphuric-hydrofluoric acid medium, and dissolution of hydrated tungsten trioxide, if present, with potassium hydroxide solution[1].

References

1. Elsie M. Donaldson, Talanta, 17, 583 (1970).

2. U. Priyadarshini and S.G. Tandon, Anal. Chem., 33, 435 (1961).

3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 458-459 (1953).

PART III

POLAROGRAPHIC METHODS

DETERMINATION OF CADMIUM IN SULPHIDE ORES AND MILL PRODUCTS

Principle

Cadmium is determined polarographically in an ammonium chloride–hydrochloric acid supporting electrolyte solution in the presence of Triton X-100 as a maximum suppressor.

Outline

The sample is decomposed with hydrochloric and nitric acids. Tin, arsenic, and antimony are subsequently removed by volatilization as the bromides from a perchloric acid medium. The solution is evaporated to dryness and the salts are dissolved in dilute hydrochloric acid. Large amounts of lead and/or copper, if present, are separated from cadmium by electrodeposition from a dilute nitric acid medium. The electrolyte is evaporated to dryness to remove nitric acid, and the salts are dissolved in dilute hydrochloric acid. The resulting solution, or the preceding solution, if large amounts of lead and/or copper are absent, is ultimately analyzed for cadmium.

Discussion of interferences

Tin, antimony, iron (III), thallium, bismuth, lead, indium, and copper produce waves, in dilute hydrochloric acid-ammonium chloride media, which are in the neighbourhood of, or precede the cadmium reduction wave. Thallium and large amounts of bismuth interfere in this method[1,2]. Small amounts of indium may interfere.

Interference from tin and antimony is avoided by volatilizing these elements, and various other elements (arsenic, mercury, and selenium), as the bromides from a hydrobromic-perchloric acid medium. Interference from iron (III) is eliminated by reducing it to the divalent state with hydroxylamine hydrochloride[1]. Small amounts of copper (up to 10 times the amount of cadmium present), bismuth, and lead; moderate amounts of nickel, cobalt, manganese, and silver; and large amounts of aluminum, zinc, magnesium, and iron (II) do not interfere[1,2]. Interference from large amounts of lead and/or copper is avoided by separating these elements from cadmium by electrodeposition.

Range

The method is suitable for samples containing approximately 0.005 to 5% of cadmium, but material containing higher concentrations can also be analyzed with reasonable accuracy.

Apparatus

Electroplating apparatus with a magnetic stirring mechanism.

Reagents

Standard cadmium solution (1 ml = 5 mg of cadmium). Dissolve 0.5000 g of pure cadmium metal by heating gently with 20 ml of 50% nitric acid. Add approximately 30 ml of water, boil the solution for several minutes to remove oxides of nitrogen, cool, and dilute to 100 ml with water. Dilute 5 ml of this stock solution to 250 ml with water (1 ml = 0.1 mg of cadmium).

Iron solution, 3% w/v. Dissolve 3 g of high-purity iron metal (cadmium-free) in 20 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, boil the solution to remove oxides of nitrogen, cool, and dilute to 100 ml with water.

Hydroxylamine hydrochloride solution, 28% w/v. Prepare fresh as required.

Triton X-100 solution, 0.1% v/v.

Nitrogen (oxygen-free).

Calibration curve

To an appropriate number of 100-ml beakers, add 2 ml of 3% iron solution (Note 1); then, by burette, add suitable varying increments of the appropriate standard 0.1 mg/ml or 5 mg/ml cadmium solution. Add 2 ml of the iron solution to a separate beaker; this constitutes the blank. Evaporate each solution to dryness, cool, wash down the sides of the beaker with approximately 5 ml of concentrated hydrochloric acid, and again evaporate the solution to dryness to ensure the complete removal of nitric acid. Cool, add 2 ml of concentrated hydrochloric acid and approximately 25 ml of water, and heat gently to dissolve the residue. Transfer the solutions to 100-ml volumetric flasks, and dilute to approximately 50 ml with water. Add concentrated ammonium hydroxide, by drops, until a slight permanent precipitate of hydrous ferric oxide is obtained, then add sufficient concentrated hydrochloric acid, by drops, to dissolve the precipitate. Add 10 ml of 28% hydroxylamine hydrochloride solution, mix, and heat the solution gently in a hot water-bath for 10-15 minutes to ensure the complete reduction of the iron. Cool, add 1 ml of 0.1% Triton X-100 solution, dilute the solution to volume with water and mix.

Transfer a suitable portion of the first of the resulting cadmium solutions to the polarographic cell, place the cell in a constant temperature-bath, and bubble nitrogen through the solution to remove dissolved air. Discontinue the flow of nitrogen, electrolyze the solution at the dropping mercury electrode from approximately -0.3 to -0.8 volt, and measure the height of the resulting cadmium wave (Note 2). Determine the wave-height for the blank and each of the remaining cadmium solutions in a similar manner, and correct the wave-height obtained for each cadmium solution by subtracting that obtained for the blank. Plot mg of cadmium vs. wave-height.

Procedures

In these procedures a reagent blank, containing 2 ml of 3% iron solution (Note 1), is carried along with the samples.

Small amounts of lead and/or copper (copper:cadmium ratio 10:1 or less) present

Transfer 0.2-1 g of powdered sample, depending on the expected cadmium content, to a 250-ml beaker. Add 10 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, cover the beaker, and boil until the decomposition of sulphide minerals is complete. Add 10 ml each of concentrated hydrobromic and perchloric acids, boil for several minutes, then remove the cover and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, add 10 ml each of concentrated hydrochloric and hydrobromic acids, and evaporate the solution to dryness (Note 3). Cool, add 2 ml of concentrated hydrochloric acid and approximately 25 ml of water to the residue, and heat gently to dissolve the soluble salts. Transfer the solution to a 100-ml volumetric flask, dilute to approximately 50 ml with water, and proceed with the neutralization and re-acidification of the solution, the reduction of iron (Notes 4 and 5), and the subsequent measurement of the cadmium wave-height as described above. Correct the wave-height obtained for the sample solution by subtracting that obtained for the blank solution, and determine the cadmium content of the sample solution by reference to the calibration curve.

Large amounts of lead and/or copper (copper:cadmium ratio more than 10:1) present

Following sample decomposition, removal of tin, arsenic, and antimony, and evaporation of the solution to dryness to remove perchloric acid as described above, add 3 ml of concentrated nitric acid and approximately 25 ml of water to the residue, and heat gently to dissolve the soluble salts. Filter the solution (Whatman No. 541 paper) into a 180-ml electrolytic beaker, and wash the beaker, paper, and residue thoroughly with water. Discard the paper and residue, and dilute the solution to approximately 100 ml with water.

Connect a clean platinum gauze cathode and a clean platinum gauze anode (Note 6) to the electroplating apparatus, lower the electrodes into the solution, and cover the beaker with a split watch glass. Turn on the stirring mechanism, and electrolyze the solution at a current of 2 amperes and an applied potential of 4-5 volts for approximately 1 hour, or until the blue colour of the copper has entirely disappeared (Note 7). Without interrupting the current, gradually raise and remove the electrodes from the solution, while directing a stream of water from a wash-bottle against the exposed part of the electrodes (Note 8). Evaporate the electrolyte to dryness, cool, wash down the sides of the beaker with approximately 10 ml of concentrated hydrochloric acid, and again evaporate the solution to dryness to ensure the complete removal of nitric acid. Add 2 ml of concentrated hydrochloric acid and approximately 25 ml of water to the residue, and heat gently to dissolve the salts. Transfer the solution to a 100-ml volumetric flask, dilute to 50 ml with water, and proceed with the determination of cadmium as described above.

Notes

1. A small amount of iron is added to the solutions employed for the preparation of the calibration curve to function as an internal indicator during the subsequent neutralization of the solutions with ammonium hydroxide.

2. Cadmium is reduced at -0.64 volt vs. the saturated calomel electrode (S.C.E.)[2].

3. If the sample contains an appreciable amount of tin, antimony, or arsenic, repeated treatment of the solution with hydrochloric and hydrobromic acids, followed by evaporation of the solution to fumes of perchloric acid is recommended to ensure the complete removal of these elements.

4. If an appreciable amount of insoluble material (e.g., silicates, lead sulphate, and lead chloride) is present, allow the solution to stand until it has settled, then use a portion of the supernatant solution for the subsequent analysis.

5. The resulting sample solution can also be used for the polarographic determination of small amounts of copper, and for the determination of small amounts of lead, provided that no lead sulphate was initially present in the sample or was formed during the decomposition of sulphide material. The half-wave potentials of the second copper wave and the lead wave in dilute ammonium chloride-hydrochloric acid media are -0.22 and -0.43 volt vs. S.C.E., respectively[2].

6. A relatively large mesh anode should be employed if an appreciable amount of lead is to be deposited.

7. Complete removal of copper and/or lead is not required. It is only necessary to reduce the concentration of these elements to a value commensurate with, or slightly greater than that of the cadmium.

8. The current should not be shut off as long as the electrodes are in the acidic solution because partial dissolution of the copper and lead oxide deposits will occur in the presence of acid.

Other applications

This method can be employed to determine cadmium (also copper and lead) in high-purity zinc metal and zinc-base die casting alloys[1]. It is also applicable to high-purity copper metal after the separation of copper by electro-deposition.

References

1. R.C. Hawkings and H.G. Thode, Ind. Eng. Chem., Anal. Ed., 16, 71 (1944).

2. I.M. Kolthoff and J.J. Lingane, "Polarography", 2nd ed., Interscience, New York, pp 519-521, 600-601 (1952).

DETERMINATION OF LEAD IN SULPHIDE ORES AND MILL PRODUCTS

Principle

Lead is determined polarographically in an ammonium chloride-hydrochloric acid supporting electrolyte solution, in the presence of Triton X-100 as a maximum suppressor, after separation from sulphate by precipitation as the mixed hydrous oxide and carbonate[1], and subsequent conversion to soluble lead nitrate.

Outline

The sample is decomposed with hydrochloric and nitric acids. Tin, arsenic, and antimony are removed by volatilization as the bromides from a perchloric acid medium, and acid-soluble lead is ultimately precipitated as the hydrous oxide, in a slightly ammoniacal medium, by occlusion with hydrous ferric oxide. Acid-insoluble lead sulphate, initially present in the sample and/or formed during the dissolution procedure, is converted to lead carbonate by the subsequent addition of ammonium carbonate. Lead is separated from the resultant ammonium sulphate, and from copper, zinc, nickel, cobalt, molybdenum, and manganese by filtration of the mixed hydrous oxide-lead carbonate precipitate. The precipitate is dissolved in nitric acid, and insoluble material is removed by filtration. The resulting filtrate is ultimately analyzed for lead.

Discussion of interferences

Tin, antimony, iron (III), thallium, bismuth, indium, and copper produce waves, in dilute hydrochloric acid-ammonium chloride media, which are in the neighbourhood of, or precede the lead reduction wave. Thallium and large amounts of bismuth interfere in this method[2,3].

Interference from tin and antimony is avoided by volatilizing these elements, and various other elements (arsenic, mercury, and selenium), as the bromides from a hydrobromic-perchloric acid medium. Interference from iron (III) is eliminated by reducing it to the divalent state with hydroxylamine hydrochloride[2].

Lead is separated from sulphate and large amounts of copper by precipitation as the mixed hydrous oxide and carbonate[1]. Small amounts of co-precipitated copper (up to 10 times the amount of lead present), bismuth, and indium, and moderate amounts of various other elements that form hydrous oxides (e.g., aluminum, gallium, and gold) or insoluble carbonates (e.g., cadmium) under the conditions employed for the separation of lead do not interfere[2,3].

Range

The method is suitable for samples containing approximately 0.005 to 5% of lead.

Reagents

Standard lead solution(1 ml = 2 mg of lead). Dissolve 0.2000 g of pure lead metal by heating gently with 20 ml of 50% nitric acid. Add approximately 30 ml of water, boil the solution for several minutes to remove oxides of nitrogen, cool, and dilute to 100 ml with water. Dilute 10 ml of this stock solution to 200 ml with water (1 ml = 0.1 mg of lead).

Iron solution, 3% w/v. Dissolve 3 g of high-purity iron metal (lead-free) in 20 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, boil the solution to remove oxides of nitrogen, cool, and dilute to 100 ml with water.

Hydroxylamine hydrochloride solution, 28% w/v. Prepare fresh as required.

Ammonium carbonate solution, saturated.

Nitric acid wash solution, 10% v/v.

Triton X-100 solution, 0.1% v/v.

Nitrogen (oxygen-free).

Calibration curve

To an appropriate number of 100-ml beakers, add 2 ml of 3% iron solution (Note 1); then, by burette, add suitable varying increments of the appropriate standard 0.1 mg/ml or 2 mg/ml lead solution. Add 2 ml of the iron solution to a separate beaker; this constitutes the blank. Evaporate each solution to dryness, cool, wash down the sides of the beaker with approximately 5 ml of concentrated hydrochloric acid, and again evaporate the solution to dryness to ensure the complete removal of nitric acid. Cool, add 2 ml of concentrated hydrochloric acid and approximately 25 ml of water, and heat gently to dissolve the residue. Transfer the solutions to 100-ml volumetric flasks, and dilute to approximately 50 ml with water. Add concentrated ammonium hydroxide, by drops, until a slight permanent precipitate of hydrous ferric oxide is obtained, then add sufficient concentrated hydrochloric acid, by drops, to dissolve the precipitate. Add 10 ml of 28% hydroxylamine hydrochloride solution, mix, and heat the solution gently in a hot water-bath for 10-15 minutes to ensure the complete reduction of the iron. Cool, add 1 ml of 0.1% Triton X-100 solution, dilute the solution to volume with water and mix.

Transfer a suitable portion of the first of the resulting lead solutions to the polarographic cell, place the cell in a constant temperature-bath, and bubble nitrogen through the solution to remove dissolved air. Discontinue the flow of nitrogen, electrolyze the solution at the dropping mercury electrode from approximately -0.1 to -0.7 volt, and measure the height of the resulting lead wave (Note 2). Determine the wave-height for the blank and each of the remaining lead solutions in a similar manner, and correct the wave-height obtained for each lead solution by subtracting that obtained for the blank. Plot mg of lead vs. wave-height.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.2-1 g of powdered sample, containing up to approximately 10 mg of lead (Note 3), to a 400-ml beaker, add 10 ml of concentrated hydrochloric acid, cover the beaker, and boil for several minutes. Add 10 ml of concentrated nitric acid, boil until most of the sulphide minerals are decomposed, then add 10 ml each of concentrated hydrobromic and perchloric acids. Boil the solution for several minutes, remove the cover, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, add 10 ml each of concentrated hydrochloric and hydrobromic acids, and allow the solution to evaporate to a paste (Note 4). Add 10 ml of concentrated nitric acid and approximately 20 ml of water, and heat to dissolve the soluble salts (Note 5).

Dilute the solution to approximately 150 ml with water and, if necessary, add sufficient 3% iron solution so that the iron content of the solution is at least 20 times that of the lead (Note 6). Add sufficient concentrated ammonium hydroxide to precipitate hydrous ferric oxide, then add several drops in excess, followed by 15 ml of saturated ammonium carbonate solution. Boil the resulting solution for several minutes to coagulate the precipitate, then filter the solution (Whatman No. 541 paper) and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the filtrate and washings.

Using a jet of hot water, transfer the bulk of the precipitate to the original beaker, add 10 ml of concentrated nitric acid, and heat gently to dissolve the precipitate (Note 7). Filter the solution through the original filter paper into a 250-ml beaker, and wash the paper and residue alternately with warm 10% nitric acid and hot water. Discard the paper and residue, and evaporate the filtrate to dryness. Cool, wash down the sides of the beaker with approximately 5 ml of concentrated hydrochloric acid, and again evaporate the solution to dryness to ensure the complete removal of nitric acid. Cool, add 2 ml of concentrated hydrochloric acid and approximately 25 ml of water to the residue, and heat gently to dissolve the salts. Transfer the solution to a 100-ml volumetric flask, dilute to approximately 50 ml with water, and proceed with the neutralization and re-acidification of the solution, the reduction of iron, and the subsequent measurement of the lead wave-height as described above.

Correct the wave-height obtained for the sample solution by subtracting that obtained for the blank solution, and determine the lead content of the sample by reference to the calibration curve.

Notes

1. A small amount of iron is added to the solutions employed for the preparation of the calibration curve to function as an internal indicator during the subsequent neutralization of the solutions with ammonium hydroxide.

2. Lead is reduced at -0.43 volt vs. the saturated calomel electrode[3].

3. Samples containing more than approximately 10 mg of lead are not recommended because of the bulkiness of the subsequent mixed hydrous oxide-lead carbonate precipitate.

4. If the sample contains an appreciable amount of tin, antimony, or arsenic, repeated treatment of the solution with hydrochloric and hydrobromic acids, followed by evaporation of the solution to fumes of perchloric acid,is recommended to ensure the complete removal of these elements.

5. Any insoluble material (e.g., silicates) that is present at this stage may be ignored because it is removed by filtration during the subsequent procedure.

6. An equivalent amount of iron solution (or approximately 1-2 ml if the solution is lead-free) should be added to the blank solution to co-precipitate possible trace amounts of lead in the reagents employed.

7. If the sample contains an appreciable amount of copper, sufficient copper may be retained in the precipitate to interfere with the determination of lead[4]. To avoid error from co-precipitated copper, dilute the solution to approximately 150 ml with water, re-precipitate the lead and iron, filter the solution through the original filter paper, then proceed as described.

References

1. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, 503, 516 (1939).

2. R.C. Hawkings and H.G. Thode, Ind. Eng. Chem., Anal. Ed., 16, 71 (1944).

3. I.M. Kolthoff and J.J. Lingane, "Polarography", 2nd ed., Interscience, New York, pp 519-521, 600-601 (1952).

4. Idem, ibid., pp 583-584 (1952).

DETERMINATION OF TELLURIUM IN COPPER SULPHIDE ORES AND MILL PRODUCTS

Principle

Tellurium is determined polarographically in a 1 M ammonium hydroxide-1 M ammonium chloride supporting electrolyte solution, in the presence of Triton X-100 as a maximum suppressor, after separation from copper by the reduction of tellurium (IV) to the elemental state with hypophosphorous acid in a 6 M hydrochloric acid medium[1,2].

Outline

The sample is decomposed with nitric and perchloric acids, and the solution is evaporated to fumes of perchloric acid to remove nitric acid and elemental sulphur. The salts are dissolved in dilute hydrochloric acid, and lead and silver chlorides and acid-insoluble material are removed by filtration. Tellurium is subsequently co-precipitated as the element with elemental arsenic, after reduction with hypophosphorous acid, and separated from copper and various other elements (nickel, cobalt, iron, manganese, zinc, and cadmium) by filtration. After dissolution of the precipitate, tellurium and arsenic are re-precipitated to remove residual copper, and the precipitate is dissolved in nitric acid. The resulting solution is ultimately analyzed for tellurium.

Discussion of interferences

Copper interferes in the determination of tellurium in ammoniacal ammonium chloride media by producing waves that precede the tellurium (IV) reduction wave, and by forming an insoluble telluride[3]. Interference from copper is eliminated by separating tellurium from this element by precipitation as elemental tellurium. Arsenic, selenium, and other elements that co-precipitate as the elements (e.g., bismuth, antimony, tin, and gold) do not interfere[1-3].

Range

The method is suitable for samples containing approximately 0.002 to 0.25% of tellurium.

Reagents

Standard tellurium solution (1 ml = 0.5 mg of tellurium). Dissolve 0.1000 g of pure tellurium metal in 20 ml of concentrated nitric acid. Add approximately 30 ml of water, boil the solution for several minutes to remove oxides of nitrogen, cool, and dilute to 200 ml with water. Dilute 20 ml of this stock solution to 200 ml with water (1 ml = 0.05 mg of tellurium).

Ammonium hydroxide-ammonium chloride solution, 2 M and 2 M, respectively. Dissolve 107 g of ammonium chloride in approximately 500 ml of water, add 133 ml of concentrated ammonium hydroxide, and dilute to 1 litre with water. Store in a polyethylene bottle.

Arsenic solution, 0.2% w/v. Dissolve 0.264 g of arsenic trioxide (As_2O_3) in 10 ml of water containing 10 pellets of sodium hydroxide, cool, and dilute to 100 ml with water.

Copper solution, 0.5% w/v. Dissolve 0.25 g of pure copper metal in 15 ml of 50% nitric acid, add 5 ml of concentrated perchloric acid, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, evaporate the solution to approximately 1-2 ml, cool, and dilute to 50 ml with water.

Bromine-hydrobromic acid solution, 10% and 90% v/v, respectively. Add 10 ml of bromine to 90 ml of concentrated hydrobromic acid and shake to dissolve.

Hypophosphorous acid-hydrochloric acid wash solution, 1% and 10% v/v, respectively.

Sulphuric acid, 50% v/v.

Hydrochloric acid, 50% v/v.

Triton X-100 solution, 0.1% v/v.

Nitrogen (oxygen-free).

Calibration curve

To an appropriate number of 100-ml beakers, add 5 ml of 50% sulphuric acid; then, by burette, add suitable varying increments of the dilute standard 0.05 mg/ml tellurium solution. Add 5 ml of 50% sulphuric acid to a separate beaker; this constitutes the blank. Evaporate each solution to fumes of sulphur trioxide, cool, wash down the sides of the beaker with a small amount of water, and evaporate the solution until most of the sulphuric acid has been removed. Cool, dissolve the residue in approximately 10 ml of water, and add 50 ml of 2 M ammonium hydroxide-2 M ammonium chloride solution and 1 ml of 0.1% Triton X-100 solution. Transfer the solutions to 100-ml volumetric flasks, dilute to volume with water and mix.

Transfer a suitable portion of the first of the resulting tellurium solutions to the polarographic cell, place the cell in a constant temperature-bath, and bubble nitrogen through the solution to remove dissolved air. Discontinue the flow of nitrogen, electrolyze the solution at the dropping mercury electrode from approximately -0.3 to -0.8 volt, and measure the height of the resulting tellurium wave (Note 1). Determine the wave-height for the blank and each of the remaining tellurium solutions in a similar manner, and correct the wave-height obtained for each tellurium solution by subtracting that obtained for the blank. Plot mg of tellurium vs. wave-height.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.2-1 g of powdered sample, depending on the expected tellurium content, to a 250-ml beaker, and add 20 ml of concentrated nitric acid and 10 ml of concentrated perchloric acid. Cover the beaker, heat gently until the decomposition of sulphide minerals is complete, then remove the cover, and evaporate the solution to dense fumes of perchloric acid to volatilize elemental sulphur. Cool, wash down the sides of the beaker with a small amount of water, and evaporate the solution to approximately 3-4 ml. Add 25 ml of water, heat the solution to the boiling point, then add 25 ml of concentrated hydrochloric acid, and boil the solution gently for several minutes. Cool the solution to 10-15°C in an ice-bath, filter it (Whatman No. 540 paper) into a 250-ml beaker, and wash the beaker, paper, and precipitate thoroughly with cold 50% hydrochloric acid. Discard the paper and precipitate.

Dilute the filtrate to approximately 125 ml with 50% hydrochloric acid, add 3 ml of 0.2% arsenic solution and 15 ml of concentrated hypophosphorous acid, cover the beaker, mix and heat the solution just to the boiling point. Allow the solution to cool to 85-90°C, and maintain it at this temperature for approximately 15 minutes. Using suction, filter the solution through a sintered-glass, medium-porosity filtering crucible, and wash the precipitate 4 or 5 times with hot 1% hypophosphorous acid-10% hydrochloric acid solution, then twice with water. Discard the filtrate and washings. Dissolve the mixed arsenic and tellurium precipitate, using approximately 10 ml of 10% bromine-90% hydrobromic acid solution, and wash the crucible 3 or 4 times with water. Collect the resulting solution in the beaker in which the precipitation was carried out. Dilute the solution to approximately 50 ml with water, and add 50 ml of concentrated hydrochloric acid and sufficient concentrated hypophosphorous acid to eliminate the brown colour imparted to the solution by the bromine. Add 15 ml in excess, and re-precipitate (Note 2), filter, and wash the precipitate as described above.

Dissolve the precipitate, using concentrated nitric acid, wash the crucible thoroughly with water, and collect the resulting solution in the same beaker. Add 5 ml of 50% sulphuric acid and evaporate the solution to fumes of sulphur trioxide (Note 3). Cool, wash down the sides of the beaker with water, evaporate the solution until most of the sulphuric acid has been removed, then dissolve the residue in water, and proceed with the addition of 2 M ammonium hydroxide-2 M ammonium chloride and Triton X-100 solutions, and the subsequent measurement of the tellurium wave-height as described above. Correct the result obtained for the sample solution by subtracting that obtained for the blank solution, and determine the tellurium content of the sample solution by reference to the calibration curve.

Notes

1. Tellurium (IV) is reduced at approximately -0.65 volt vs. the saturated calomel electrode (S.C.E.)[3].

2. Copper, in small amounts, catalyzes and hastens the reduction of arsenic and tellurium with hypophosphorous acid[1]. If re-precipitation of the arsenic and tellurium appears to be slow or incomplete at this stage, add 2-3 drops of 0.5% copper solution.

3. Because selenium is partly volatilized from sulphuric acid solutions that are evaporated to near dryness[4], it can probably be determined simultaneously in the resulting ammoniacal ammonium chloride sample solution if perchloric acid, rather than sulphuric acid, is employed for the removal of the nitric acid[2]. The half-wave potential of the selenium wave, corresponding to the reduction of selenium (IV) to the -2 state, occurs at approximately -1.5 volts vs. S.C.E.[3].

Other applications

This method can be employed to determine tellurium in copper metal and alloys[1]. It should be applicable to various other sulphide ores (e.g., nickel, cobalt, iron, manganese, zinc, and cadmium) and mill products if a small amount of copper is added during the precipitation stages to catalyze the reduction of tellurium and arsenic.

References

1. K.J. Cathro, Aust. J. Appl. Sci., 9, 255 (1958).

2. C.L. Luke, Anal. Chem., 31, 572 (1959).

3. J.J. Lingane and L.W. Niedrach, J. Am. Chem. Soc., 71, 196 (1949).

4. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 7, 149 (1961).

DETERMINATION OF TIN IN ORES AND MILL PRODUCTS

Principle

This method is a modification of that developed by Faye and McMaster[1], and involves the separation of tin from certain matrix elements by precipitation as the sulphide and hydrous oxide. Tin is determined polarographically, in the presence of Triton X-100 as a maximum suppressor, by measurement of the second chlorostannate ion reduction wave in a 2 M hydrochloric acid-3 M ammonium chloride supporting electrolyte solution.

Outline

The sample is decomposed by fusion with sodium carbonate and sodium peroxide, and the melt is digested in water. Tin and various elements of the copper and arsenic groups that may be present in the sample are ultimately co-precipitated as the sulphides with molybdenum sulphide, in a dilute hydrochloric-tartaric acid medium, and separated from iron, chromium, tungsten, niobium, tantalum, titanium, zirconium, zinc, indium, thallium, vanadium, uranium, and aluminum by filtration. The mixed sulphide precipitate is dissolved in nitric and sulphuric acids, and lead sulphate is ultimately removed by filtration. Tin is subsequently co-precipitated as the hydrous oxide with hydrous aluminum oxide from a weakly ammoniacal medium, and separated from molybdenum, copper, silver, cadmium, and the platinum group metals by filtration. The resultant mixed hydrous oxide precipitate is dissolved in dilute hydrochloric acid. The resulting solution is analyzed for tin.

Discussion of interferences

Copper, lead, nickel, tungsten, vanadium, iron, arsenic, bismuth, and antimony produce waves in 4 M or greater chloride ion media, which are in the neighbourhood of, or precede the double chlorostannate ion reduction wave[2-4].

Interference from lead, which is reduced at almost the same potential as tin (IV)[3,4], is avoided by separating it as the insoluble sulphate. Interference from nickel, tungsten, vanadium, and iron is eliminated by separating tin from these elements by co-precipitation as the sulphide with molybdenum sulphide in a 0.25 M hydrochloric-tartaric acid medium[5,6]. Tin is separated from copper by co-precipitation as the hydrous oxide with hydrous aluminum oxide from a weakly ammoniacal medium[3,6]. Small amounts of bismuth, arsenic, and antimony (equal to the amount of tin present), residual iron, and other elements that are not completely separated from tin by the described procedures (e.g., gold and mercury) do not interfere in the determination of tin[1,3,4].

Range

The method is suitable for samples containing approximately 0.005 to 5% of tin.

Reagents

Standard tin solution (1 ml = 0.5 mg of tin). Dissolve 0.1000 g of pure granulated tin metal by heating with 20 ml of concentrated sulphuric acid. Cool, cautiously transfer the solution, in small portions, to a 200-ml volumetric flask containing 100 ml of 20% sulphuric acid, mix, and cool to room temperature. Dilute the resulting solution to approximately 190 ml with water, mix, cool to room temperature, and dilute to volume with water. Dilute 20 ml of this stock solution to 100 ml with 20% sulphuric acid (1 ml = 0.1 mg of tin).

Ammonium molybdate solution, 1% w/v. Dissolve 1 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in approximately 50 ml of warm water, cool, and dilute to 100 ml.

Aluminum sulphate solution, 4% w/v. Dissolve 8 g of the anhydrous reagent (or 11.8 g of the nonahydrate reagent) in approximately 150 ml of warm water, cool, and dilute to 200 ml.

Hydrochloric acid, 4 M. Dilute 342 ml of concentrated hydrochloric acid to 1 litre with water.

Sulphuric acid, 20% v/v.

Ammonium hydroxide, 50% v/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% hydrochloric acid saturated with hydrogen sulphide.

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Triton X-100 solution, 0.1% v/v.

Nitrogen (oxygen-free).

Calibration curve

To an appropriate number of 400-ml beakers, add, by burette, suitable varying increments of the appropriate standard 0.1 mg/ml or 0.5 mg/ml tin solution, and dilute each solution to 50 ml with 20% sulphuric acid. Add 50 ml of 20% sulphuric acid to a separate beaker; this constitutes the blank. Dilute each solution to approximately 150 ml with water, heat almost to the boiling point, and add several drops of 0.1% methyl red solution and 4 ml of 4% aluminum sulphate solution. Carefully neutralize the solution with 50% ammonium hydroxide, and add several drops in excess (Note 1). Allow the precipitate to settle, then filter the solution (Whatman No. 541 paper) and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the filtrate and washings.

Dissolve the precipitate, using 50 ml of warm 4 M hydrochloric acid, wash the paper twice with 6-8 ml of hot water, and collect the resulting solution in the original beaker. Transfer the solutions to 100-ml volumetric flasks containing 16 g of ammonium chloride, and shake gently until the salt has dissolved. Warm the solutions to room temperature, add 1 ml of 0.1% Triton X-100 solution, dilute to volume with water and mix.

Transfer a suitable portion of the first of the resulting tin solutions to the polarographic cell, place the cell in a constant temperature-bath, and bubble nitrogen through the solution to remove dissolved air. Discontinue the flow of nitrogen, electrolyze the solution at the dropping mercury electrode from approximately -0.1 to -0.8 volt, and measure the height of the second tin wave (Note 2). Determine the wave-height for the blank and each of the remaining tin solutions in a similar manner, and correct the wave-height obtained for each tin solution by subtracting that obtained for the blank. Plot mg of tin vs. wave-height.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.2-1 g of powdered sample, containing up to approximately 10 mg of tin (Note 3), to a 50-ml zirconium crucible, add 1 g of sodium carbonate and 7-8 g of sodium peroxide and mix thoroughly. Fuse the mixture over a blast burner, and keep the melt at red heat for several minutes to ensure complete sample decomposition. Allow the melt to cool, then transfer the crucible and contents to a 600-ml (covered) beaker containing 100 ml of water. When the subsequent reaction has ceased, remove the crucible after washing it thoroughly with hot water, and boil the solution for approximately 10 minutes to remove the residual peroxide. Add 10 g of tartaric acid, stir to dissolve, then neutralize the solution approximately with concentrated hydrochloric acid, and add a sufficient excess to clarify the solution. Add several drops of 0.1% methyl red solution (Notes 4 and 5), carefully neutralize the solution with 50% ammonium hydroxide, then add 10 ml of concentrated hydrochloric acid and 2 ml of 1% ammonium molybdate solution (Note 6), and dilute the solution to approximately 450 ml with water. Pass hydrogen sulphide through the resulting solution for 1 hour, allow the precipitate to settle for approximately 2 hours, then filter the solution (Whatman No. 32 paper and paper pulp) and wash the beaker, paper, and precipitate thoroughly with hydrogen sulphide wash solution. Discard the filtrate and washings.

Transfer the paper and precipitate to the original beaker, add 25 ml of concentrated nitric acid, and carefully add 10 ml of concentrated sulphuric acid in small portions. Cover the beaker, heat gently to destroy the paper and pulp, then evaporate the solution to fumes of sulphur trioxide. Repeat the nitric acid treatment and the subsequent evaporation of the solution to fumes of sulphur trioxide until all of the organic material has been destroyed. Cool the solution, remove the cover, carefully add 100 ml of water in small portions, and heat gently to dissolve the soluble salts. If lead sulphate is present, cool the solution in an ice-bath, filter it (Whatman No. 40 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with cold water. Discard the paper and precipitate.

Dilute the filtrate to approximately 150 ml with water, and heat the solution almost to the boiling point. Add several drops of 0.1% methyl red solution (Note 4) and 4 ml of 4% aluminum sulphate solution (Note 7), and proceed with the precipitation, filtration, and dissolution of the mixed tin and aluminum hydrous oxide precipitate, and the subsequent measurement of the tin wave-height as described above. Correct the wave-height obtained for the sample solution by subtracting that obtained for the blank solution, and determine the tin content of the sample solution by reference to the calibration curve.

Notes

1. The addition of a large excess of ammonium hydroxide should be avoided because the hydrous oxides of tin and aluminum are partly soluble in moderately ammoniacal solution[3].

2. Stannic tin is reduced in two stages in 2 M hydrochloric acid-3 M ammonium chloride media, but only the second step, corresponding to the reduction of chlorostannite ion to the metal, at approximately -0.6 volt vs. the saturated calomel electrode (S.C.E.), is suitable for the determination of tin. The half-wave potential of the first tin wave, corresponding to the reduction of hexachlorostannate ion to chlorostannite ion, occurs at approximately -0.25 volt vs. S.C.E.[2].

3. Samples containing more than approximately 10 mg of tin are not recommended because the slimy character of the subsequent tin sulphide precipitate renders filtration and washing difficult[6].

4. If the solution contains an appreciable amount of coloured ions (e.g., copper, nickel, and/or chromium), litmus paper can be employed as indicator during the neutralization step.

5. Any insoluble hydrated tungsten trioxide that may be present at this stage can be dissolved by adding an excess of ammonium hydroxide and warming the solution. The excess ammonium hydroxide should subsequently be neutralized with concentrated hydrochloric acid.

6. The addition of ammonium molybdate solution can be omitted if the sample is known to contain approximately 10 mg or more of molybdenum.

7. Although aluminum is added primarily for the co-precipitation and subsequent separation of tin as the hydrous oxide, it also provides a hydrous oxide matrix which allows the hydrous oxide of stannic tin to be readily dissolved by warm dilute hydrochloric acid[1]. In the absence of such a matrix, some tin may be retained in the fibres of the filter paper[6].

Other applications

With modifications in the decomposition procedure, this method can be employed to determine tin in steels[1].

References

1. G.H. Faye and C.H. McMaster, "A Polarographic Determination of Tin in Steel", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Mines Branch Research Report MD 144, May (1953).

2. J.J. Lingane, J. Am. Chem. Soc., 67, 919 (1945).

3. E.M. Godar and O.R. Alexander, Ind. Eng. Chem., Anal. Ed., 18, 681 (1946).

4. D.L. Love and S.C. Sun, Anal. Chem., 27, 1557 (1955).

5. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 49-58 (1938).

6. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 287-288, 295 (1953).

DETERMINATION OF ZINC IN ZINC SULPHIDE CONCENTRATES (RAPID CONTROL METHOD)

Principle

Zinc is determined polarographically in a 1 M ammonium hydroxide-0.5 M ammonium chloride supporting electrolyte solution in the presence of Triton X-100 as a maximum suppressor[1].

Outline

The sample is decomposed with hydrochloric, nitric, and perchloric acids, and the solution is evaporated to fumes of perchloric acid to remove nitric acid and elemental sulphur. The resulting solution is analyzed for zinc.

Discussion of interferences

Copper, cadmium, and nickel produce waves, in ammoniacal ammonium chloride media, which precede the zinc reduction wave[2], but none of these elements normally interfere in this method because they are not usually present in zinc sulphide concentrates. Iron (III) does not interfere because it is precipitated as the hydrous oxide in the supporting electrolyte solution employed for the determination of zinc.

Range

The method is suitable, provided high accuracy is not required, for the routine determination of approximately 50 to 60% of zinc in sulphide concentrates.

Reagents

Standard zinc solution (1 ml = 0.5 mg of zinc). Dissolve 0.5000 g of pure zinc metal in 50 ml of 20% hydrochloric acid, and dilute to 1 litre with water.

Ammonium hydroxide-ammonium chloride solution, 2M and 1 M, respectively. Dissolve 53.5 g of ammonium chloride in approximately 500 ml of water, add 133 ml of concentrated ammonium hydroxide, and dilute to 1 litre with water. Store in a polyethylene bottle.

Triton X-100 solution, 0.1% v/v.

Nitrogen (oxygen-free).

Calibration curve

To an appropriate number of 100-ml volumetric flasks, add 50 ml of 2 M ammonium hydroxide-1 M ammonium chloride solution, and 1 ml of 0.1% Triton X-100 solution; then, by burette, add suitable varying increments of the standard 0.5 mg/ml zinc solution. Dilute each solution to volume with water and mix.

Transfer a suitable portion of the first of the resulting zinc solutions to the polarographic cell, place the cell in a constant temperature-bath, and bubble nitrogen through the solution to remove dissolved air. Discontinue the flow of nitrogen, electrolyze the solution at the dropping mercury electrode from approximately -1.0 to -1.65 volts, and measure the height of the resulting zinc wave (Notes 1 and 2). Determine the wave-height for each of the remaining zinc solutions in a similar manner, and plot mg of zinc vs. wave-height.

Procedure

Transfer 0.25 g of powdered sample to a 250-ml beaker, add 5 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid, cover the beaker, and heat gently until the decomposition of sulphide minerals is complete. Remove the cover, wash down the sides of the beaker with a small amount of water, add 3 ml of concentrated perchloric acid, and evaporate the solution to dense fumes of perchloric acid to volatilize elemental sulphur. Cool, add approximately 50 ml of water, and heat gently to dissolve the soluble salts. Cool the solution to room temperature, transfer it to a 250-ml volumetric flask, dilute to volume with water and mix.

Transfer a 10-ml aliquot to a 100-ml volumetric flask, and add 50 ml of 2 M ammonium hydroxide-1 M ammonium chloride solution and 1 ml of 0.1% Triton X-100 solution. Dilute the solution to volume with water, mix, and proceed with the subsequent measurement of the zinc wave-height as described above. Determine the zinc content of the aliquot by reference to the calibration curve.

Notes

1. Zinc is reduced at -1.32 volts vs. the saturated calomel electrode[1].

2. For rapid control work, in which speed is essential, an instrument with a fast polarization rate (e.g., a cathode-ray polarograph) can be advantageously employed in this method. The zinc wave-height can also be determined relatively quickly with a manual polarograph by recording only two points - the first on the residual current portion of the curve - the second on the diffusion current plateau[1].

References

1. C.H. McMaster, "The Application of Polarography as a Rapid Control Method in the Determination of Zinc in Zinc Concentrates", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Mines Branch Investigation Report IR 63-53, May (1963).

2. I.M. Kolthoff and J.J. Lingane, "Polarography", 2nd ed., Interscience, New York, pp 503-505, 582, 605 (1952).

PART IV

GRAVIMETRIC METHODS

DETERMINATION OF ALUMINUM IN ACID-SOLUBLE AND REFRACTORY SILICATE ROCKS AND MINERALS, CARBONATE ROCKS, CLAY, AND SHALE BY PRECIPITATION WITH AMMONIUM HYDROXIDE

Principle

Aluminum is determined by weighing as the oxide, after precipitation as the hydrous oxide with ammonium hydroxide from an approximately neutral (pH 6.5-7.5) ammonium chloride medium[1].

Outline

Acid-soluble silicate rocks and minerals, clay, and shale are decomposed with hydrofluoric, hydrochloric, and sulphuric acids, and the solution is evaporated to fumes of sulphur trioxide to remove silica and excess hydrofluoric acid. Acid-insoluble material, if present, is ultimately separated by filtration, ignited, and fused with sodium carbonate. The melt is dissolved in the initial filtrate, and iron, titanium, and other interfering elements (zirconium, molybdenum, and vanadium) are separated from aluminum by chloroform extraction of their cupferron complexes. The aluminium in the aqueous phase is ultimately precipitated as the hydrous oxide with ammonium hydroxide, and separated from calcium, magnesium, manganese, sodium, potassium, and chromium (VI) by filtration. After dissolution of the precipitate, aluminum is re-precipitated to remove occluded elements, and the precipitate is ignited, and weighed.

Refractory silicate rocks and minerals are decomposed by fusion with sodium carbonate, and the melt is dissolved in dilute sulphuric acid. Silica is removed by volatilization as silicon tetrafluoride, and aluminum, iron, titanium, and zirconium are ultimately precipitated as the hydrous oxides with ammonium hydroxide, and separated from the excess sodium salts, calcium, magnesium, manganese, and other elements mentioned above by filtration. The mixed hydrous oxide (R_2O_3) precipitate is dissolved in dilute hydrochloric acid, and the hydrous oxides are re-precipitated to remove some occluded elements. After dissolution of the precipitate, iron, titanium, and other co-precipitated or occluded elements (zirconium, vanadium, and molybdenum) are separated from aluminum by chloroform extraction of their cupferron complexes. The aluminum in the resulting aqueous phase is ultimately precipitated with ammonium hydroxide, and determined as described above.

Alternatively, following sample decomposition by fusion with sodium carbonate and the separation of silica by double dehydration with perchloric acid as described in the Classical-Gravimetric Method for silica (Procedure C (a), p 201, Note 27), aluminum can be determined in the above materials as follows:

> The ignited residue remaining after the volatilization of silica is fused with sodium carbonate. The melt is dissolved in the filtrate from the silica determination, and fluoride, if present, is removed by evaporation of the resulting solution with sulphuric acid. The mixed hydrous oxides (R_2O_3) are ultimately precipitated twice with ammonium hydroxide, and aluminum is subsequently determined by the method described for refractory silicate rocks and minerals.

Carbonate rocks are analyzed for aluminum by the alternative method described above for refractory and acid-soluble silicate rocks and minerals, clay, and shale, following sample decomposition with hydrochloric, nitric, and perchloric acids, and the separation of silica by double dehydration with perchloric acid as described in the Classical-Gravimetric Method for silica (Procedure D, p 201, Note 31).

Discussion of interferences

Various elements interfere in the determination of aluminum by precipitation as the hydrous oxide with ammonium hydroxide because they form insoluble hydrous oxides [iron (III), titanium, zirconium, niobium, tantalum, bismuth, chromium (III), beryllium, lead, and tin], or because they are occluded (vanadium, silica, phosphate, molybdenum, tungsten, arsenic, antimony, copper, zinc, cobalt, nickel, cadmium, silver, gold and the platinum metals) by the gelatinous precipitate[1-4]. Phosphate, if present in excess of that required to combine stoichiometrically with the aluminum present, and carbonate, and arsenate react with calcium and magnesium to form insoluble compounds that contaminate the precipitate[1,3]. Fluoride prevents the complete precipitation of aluminum with ammonium hydroxide because it forms a stable fluo complex with aluminum[5].

Fluoride, if present in the sample, or hydrofluoric acid employed for sample decomposition, are removed by repeated evaporation of the sample solution with sulphuric acid. Co-precipitation and/or occlusion of iron, titanium, vanadium, zirconium, tin, and molybdenum is avoided by separating these elements from aluminum by chloroform extraction of their cupferron complexes . Interference from various copper and arsenic group elements [e.g., copper, silver, arsenic (III), antimony, gold, bismuth, cadmium, molybdenum, platinum, palladium, and tin], if present in significant amounts, can be eliminated by separating these elements from aluminum by precipitation with hydrogen sulphide from an approximately 0.3 M sulphuric acid medium[1,3,6]. Calcium and magnesium are prevented from co-precipitating as the hydrous oxides or insoluble carbonates by precipitating the aluminum from an ammonium chloride medium, and by employing carbonate-free ammonium hydroxide, respectively. Chromium (III) can be prevented from co-precipitating as the hydrous oxide by oxidizing it to the hexavalent state by evaporation with perchloric acid; chromium (VI) does not form a hydrous oxide with ammonium hydroxide[1].

Re-precipitation of the aluminum, after dissolution of the initial precipitate in dilute hydrochloric acid, eliminates positive error from calcium, magnesium, manganese, cobalt, nickel, sodium, and potassium, which are occluded, in small amounts, by the initial precipitate[1].

Contamination of the aluminum precipitate with calcium and magnesium phosphates, if an excess amount of phosphate is present, can be avoided by adding a sufficient excess of iron (III), prior to the precipitation of aluminum, to occlude the phosphate, followed by a double precipitation of the mixed hydrous oxides of iron and aluminum, dissolution of the precipitate, separation of the iron from aluminum by cupferron-chloroform extraction, and subsequent re-precipitation of the aluminum[7]. Phosphate causes high results for aluminum because, depending on the amount of aluminum present, it is completely or partly occluded by the aluminum precipitate, and is subsequently converted to the pentoxide during the ignition of the precipitate[1,3,6]. Positive error from phosphate can be obviated by fusing the ignited residue with sodium carbonate, determining its phosphorus pentoxide content spectrophotometrically, and subtracting the amount obtained from the weight of the ignited residue.

If silica has been separated by acid dehydration, the ignited residue is usually contaminated with a small amount of silica. Positive error from silica can be eliminated by treating the ignited residue with hydrofluoric and sulphuric acids, and evaporating to dryness to volatilize silicon as the tetrafluoride, followed by re-ignition and weighing of the residue[1].

Beryllium is not separated from aluminum by any of the separation procedures described and causes high results for aluminum. Niobium, tantalum, uranium, thorium, gallium, indium and the rare earth elements also interfere in this method[2,5].

Range

The method is suitable for samples containing more than approximately 0.1% of aluminum.

Reagents

Cupferron solution, 9% w/v. Prepare fresh as required, and filter the solution, if necessary.

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Concentrated ammonium hydroxide (carbonate-free). If a carbonate-free commercial product is not available, a pure solution (approximately 15 M) can be prepared by saturating freshly boiled and cooled water with ammonia gas.

Iron solution, 1% w/v. Dissolve 1 g of high-purity iron metal (aluminum-free) in 10 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, and dilute the solution to 100 ml with water.

Ammonium hydroxide (carbonate-free), 20% v/v.

Sulphuric acid, 50% v/v.

Hydrochloric acid, 50% and 2% v/v.

Ammonium chloride wash solution, 2% w/v. Dissolve 20 g of the reagent in approximately 300 ml of water, add 3 drops of concentrated, carbonate-free ammonium hydroxide, and dilute to 1 litre with water.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% sulphuric acid saturated with hydrogen sulphide.

Chloroform. Analytical reagent-grade.

Procedures

In these procedures a reagent blank is carried along with the samples if the expected aluminum content is approximately 5% or less.

A - Acid-soluble silicate rocks and minerals, clay, and shale

Transfer 0.5-1 g of powdered sample (Note 1), containing up to approximately 100 mg of aluminum, to a 100-ml platinum dish, moisten with several ml of water, and add 15 ml of concentrated hydrofluoric acid. Allow the mixture to digest at room temperature for approximately 30 minutes, then add 10 ml of concentrated hydrochloric acid and 15 ml of 50% sulphuric acid, and evaporate the solution to fumes of sulphur trioxide (Note 2). Cool, add 10 ml each of water and concentrated hydrofluoric and hydrochloric acids, and evaporate the solution to fumes again. If necessary, repeat the addition of water and concentrated hydrofluoric and hydrochloric acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water, evaporate the solution to fumes, then repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid. Cool, add approximately 40 ml of water, and heat gently until the solution becomes clear (Notes 3-5).

Transfer the resulting solution to a 250-ml separatory funnel, and add sufficient 50% sulphuric acid so that approximately 10 ml of the concentrated acid are present. Dilute to approximately 100 ml with water, and cool the solution to about 10°C in an ice-bath. Add sufficient cold 9% cupferron solution (Note 6) to precipitate iron, titanium, and various other elements that may be present (vanadium, molybdenum, and zirconium), mix, stopper, and extract the cupferrates by repeated shaking, for 1 minute each time, with two 30-ml, and then three or more 15-ml portions of chloroform until the organic layer is colourless. Discard each extract. Transfer the aqueous phase to a 400-ml beaker, warm gently to remove residual chloroform, then evaporate the solution to approximately 50 ml. Cover the beaker, add 10 ml each of concentrated nitric and hydrochloric acids and, if chromium is present, add 5 ml of concentrated perchloric acid, and boil the solution for 20-30 minutes to destroy organic material. Cool, remove the cover and, depending on the absence or presence of chromium, evaporate the solution to fumes of sulphur trioxide or to fumes of perchloric acid, respectively. If organic material is still present, repeat the treatment with nitric and hydrochloric acids, then evaporate the solution to approximately 5 ml (Note 7). Cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid, heat gently to dissolve the salts and, if necessary, filter the solution (Whatman No. 541 paper) into a 400-ml beaker to remove residual silica (Note 8) and/or barium sulphate. Wash the beaker, paper, and residue thoroughly with warm 2% hydrochloric acid and warm water, and discard the paper and residue.

Dilute the resulting solution to approximately 200 ml with water (Note 9), and add several drops of 0.1% methyl red solution. Neutralize the solution approximately with concentrated carbonate-free ammonium hydroxide (Note 10), and add several drops in excess. Heat the solution to the boiling point, add 50% hydrochloric acid, by drops, until the colour of the solution changes to a faint pink, then add 20% carbonate-free ammonium hydroxide, by drops, until the colour changes to a distinct canary yellow (Note 11). Boil the solution for approximately 30 seconds to coagulate the resulting aluminum hydrous oxide precipitate, allow the precipitate to settle for about 1 minute, then, without delay (Note 12), filter the solution (Whatman No. 541 paper) into an 800-ml beaker, and wash the beaker, paper, and precipitate 4 or 5 times with hot 2% ammonium chloride solution (Note 13).

Using a jet of hot water, carefully transfer the precipitate to the beaker in which the precipitation was carried out, add 7 ml of concentrated hydrochloric acid, and heat gently to dissolve the precipitate. Dilute the solution to approximately 150 ml with water, and re-precipitate the aluminum as described above. Filter the solution through the original filter paper, and collect the filtrate in the beaker containing the initial filtrate. Transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate 8 times with hot 2% ammonium chloride solution (Notes 14-16).

Transfer the paper and precipitate to a tared 30-ml Alundum crucible (Note 17), and burn off the paper at a low temperature in a muffle furnace. Ignite the precipitate at 1200°C (Note 18) for 1 hour, cool in a dessicator and weigh (Note 19). Repeat the ignition and weighing until constant weight is obtained, and correct the result obtained for the sample by subtracting that obtained for the reagent blank.

B - <u>Refractory silicate rocks and minerals</u>

Transfer 0.5-1 g of powdered sample (Note 20), containing up to approximately 100 mg of aluminum, to a 30-ml platinum crucible, and ignite in a muffle furnace at 800-900°C for approximately 30 minutes (Note 21). Cool the crucible, add a five-fold weight excess of sodium carbonate, mix, and cover the mixture with 0.5-1 g of sodium carbonate. Cover the crucible with a platinum cover, heat at a low temperature for 5-10 minutes, then fuse the mixture at 900-1000°C for approximately 30 minutes. Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, and allow the crucible and contents to cool. Transfer the crucible and cover to a 400-ml (covered) Teflon beaker containing approximately 30 ml of water, and add 30 ml of 50% sulphuric acid in small portions. When dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with hot water. Add 10 ml of concentrated hydrofluoric acid, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, evaporate the solution to fumes again, then repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid. Evaporate the resulting solution to approximately 5 ml or until the sodium salts begin to crystallize, cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid, and heat gently to dissolve the salts (Note 3).

Transfer the solution to a 400-ml pyrex beaker, dilute to approximately 200 ml with water, and precipitate the mixed hydrous oxides (R_2O_3) of aluminum, iron, and other elements that may be present (titanium, and zirconium) twice with ammonium hydroxide as described in Procedure A (Notes 14, 15, 22 and 23).

Transfer the paper and precipitate (Note 24) to the beaker in which the precipitation was carried out, place the beaker under the funnel, and wash the funnel with hot 5% hydrochloric acid. Add 40 ml of 50% sulphuric acid and 10 ml each of concentrated nitric and hydrochloric acids, and macerate the paper with a stirring rod. Cover the beaker, and boil the solution for 20-30 minutes to decompose the paper. Cool, remove the cover, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with a small amount of water, add 10 ml each of concentrated nitric and hydrochloric acids, evaporate the solution to fumes again, and continue the nitric-hydrochloric acid treatment and the subsequent evaporation to fumes until the filter paper has been completely destroyed and the yellow colour due to carbonaceous material has disappeared. Evaporate the solution to approximately 10 ml, cool, and add 40 ml of water. If necessary, heat gently to clarify the solution, transfer it to a 250-ml separatory funnel, and dilute to approximately 100 ml with water. Cool the solution to 10°C in an ice-bath, then proceed, as described in Procedure A, with the cupferron-chloroform extraction of iron, titanium, and zirconium, and the subsequent destruction of the excess cupferron in the aqueous phase with hydrochloric and nitric acids. Evaporate the resulting solution to approximately 5 ml (Note 7), cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid and, if necessary, heat gently to clarify the solution.

Dilute the solution to approximately 150 ml with water, and precipitate and filter the hydrous oxide of aluminum once as described in Procedure A. Transfer the precipitate quantitatively to the filter paper (Note 17), wash the paper and precipitate 8 times with hot 2% ammonium chloride solution, then transfer the paper and precipitate to a tared Alundum crucible, and proceed with the ignition and weighing of the crucible and ignited precipitate as described above.

C - Refractory and acid-soluble silicate rocks and minerals, clay, and shale after the separation of silica

Following sample decomposition by fusion with sodium carbonate, and the separation of silica by double dehydration of silicic acid with perchloric acid, as described in Procedure C (a) (p 201, Note 27) of the Classical-Gravimetric Method for silica, add 0.5 g of sodium carbonate to the ignited residue remaining in the platinum crucible after the volatilization of silica. Cover the crucible, and fuse the mixture over a blast burner until a clear melt is obtained. Cool, and tranfer the crucible and cover to the beaker (covered) containing the filtrate from the silica separation. When dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with hot water, and evaporate (Note 25) the resulting solution to approximately 5 ml or until the sodium salts begin to crystallize. Cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid, heat gently to dissolve the salts and, if necessary, filter the solution (Whatman No. 541 paper) into a 400-ml beaker to remove residual silica. Wash the beaker, paper, and residue thoroughly with hot 2% hydrochloric acid and hot water, and discard the paper and residue.

Dilute the resulting solution to approximately 200 ml with water, then proceed with the ammonium hydroxide precipitation of the mixed hydrous oxides (R_2O_3) of aluminum, iron and other elements, and the subsequent determination of aluminum as described in Procedure B (Note 26).

D - Carbonate rocks after the separation of silica

Following sample decomposition with hydrochloric, nitric and perchloric acids, and the separation of silica by double dehydration with perchloric acid as described in Procedure D (p 201, Note 31) of the Classical-Gravimetric Method for silica, determine aluminum by the method described in Procedure C (Notes 26-28).

Notes

1. Aluminum can be determined in acid-soluble silicate rocks and minerals, clay, and shale by the method described in Procedure C, but this procedure is shorter and more rapid, and is directly applicable to samples containing fluoride (cf., Procedure C, Note 25).

2. The sample solution should not be allowed to evaporate to dryness. This results in the formation of anhydrous aluminum compounds, which are virtually insoluble in water or dilute acid, and causes low results for aluminum[8].

3. If the sample contains an appreciable amount of calcium, prolonged heating and greater dilution of the solution may be necessary at this stage to obtain complete dissolution of calcium sulphate.

4. If any acid-insoluble residue is present, it should be quantitatively removed by filtration, ignited at about 750°C in a platinum crucible, and fused with 0.5-1 g of sodium carbonate. The melt should subsequently be dissolved in the initial solution.

5. If the sample contains an appreciable amount of aluminum, and a 1-g sample has been taken for analysis, both aluminum and iron (Procedure B, p 279, of the Volumetric-Stannous Chloride-Dichromate Method for total iron) can be determined at this stage, if the sample solution is diluted to a definite volume with water, and suitable aliquots are taken for the respective analyses.

6. Approximately 2-2.5 ml of 9% cupferron solution are usually sufficient for the complexation of 10 mg of metal ion. To test for completeness of precipitation, extract the solution twice with chloroform, then add 1-2 ml of cupferron solution. Complete precipitation is indicated by a transient white precipitate resulting from the presence of excess cupferron.

7. Silicate rocks, and clay and shale usually contain only negligible amounts of heavy metals (i.e., the copper and arsenic group elements) and, consequently, the separation of these elements, prior to the precipitation of aluminum with ammonium hydroxide, can generally be omitted. However, if moderate amounts of these elements are present in the sample, they should be removed at this stage by precipitation with hydrogen sulphide[6] as follows:

Evaporate the solution to approximately 3 ml (Note 2), cool, and dilute to about 200 ml with water. Heat to the boiling point, pass hydrogen sulphide through the solution for approximately 30 minutes, then filter the solution (Whatman No. 32 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hydrogen sulphide wash solution. Discard the paper and precipitate. Boil the filtrate to expel hydrogen sulphide, and evaporate the solution to approximately 200 ml. If necessary, filter the solution to remove coagulated sulphur, add 10 ml of concentrated hydrochloric acid, then proceed as described.

8. Silica should not be present at this stage unless acid-insoluble residue, remaining after sample decomposition, was fused with sodium carbonate (Note 4). If heavy metals were removed by precipitation with hydrogen sulphide (Note 7), any silica and/or barium sulphate present would be removed with the mixed sulphide precipitate during filtration of the sample solution.

9. If the sample contains phosphate in amounts approximately equal to, or in excess of that required to combine stoichiometrically with the aluminum present [i.e., 1 mg of aluminum = 2.63 mg of phosphorus pentoxide (P_2O_5)], some iron (III) solution should be added at this stage as a collector for phosphate. If iron is not added under these conditions, calcium and magnesium will co-precipitate as insoluble phosphates during the ammonium hydroxide separation of aluminum, and contaminate the aluminum hydrous oxide precipitate. This also causes low results for calcium and magnesium if they are to be determined in the filtrate remaining after the ammonium hydroxide separation procedure (Note 15). Approximately a ten-fold excess of iron (III) (i.e., 1 ml of a 1% solution) should be added for every mg of excess phosphate (as phosphorus pentoxide) present[1,7]. The precipitation of the mixed hydrous oxides of aluminum and iron, and the subsequent determination of aluminum should then be completed as described in Procedure B.

10. The ammonium hydroxide employed for the precipitation of the aluminum should not contain carbonates because magnesium and calcium will co-precipitate as insoluble carbonates and contaminate the aluminum hydrous oxide precipitate[1,3]. This also causes low results for calcium and magnesium if they are to be determined in the filtrate remaining after the ammonium hydroxide separation procedure (Note 15).

11. Particular care must be taken in adjusting the end-point. The precipitation of aluminum is incomplete if insufficient ammonium hydroxide is employed, and an excess results in loss of aluminum because of the partial re-dissolution of the precipitate[1,2]. The use of dilute hydrochloric acid, before the final adjustment of the end-point, makes the colour change, in the presence of the precipitate, easier to observe. If the colour of the solution changes to orange, during or after the subsequent boiling stage to coagulate the precipitate, the end-point should be re-adjusted with dilute 20% ammonium hydroxide.

12. The time-lapse between the precipitation and filtration should be kept to a minimum to avoid air-oxidation and subsequent co-precipitation of manganese as the dioxide.

13. Hot water should not be used to wash the precipitate. This results in loss of aluminum because of the conversion (i.e., peptization) of the hydrous oxide to the colloidal state[1,3].

14. If the sample contains an appreciable amount of magnesium, it may be advisable to re-dissolve the precipitate and re-precipitate the aluminum again to remove occluded magnesium[3,6].

15. The combined filtrates and washings can be used for the determination of calcium and magnesium by the Volumetric-Oxalate (p 243) and the Gravimetric-Pyrophosphate (p 182) Methods, respectively.

16. Except in the most exact work, the small amount of aluminum that may remain in the combined filtrates and washings may be neglected. In exact work, this residual aluminum may be recovered, after the destruction of excess ammonium salts, as follows[3,6]:

Acidify the combined filtrates and washings with concentrated hydrochloric acid, and evaporate the solution to approximately 100 ml. Add 50 ml of concentrated nitric acid, cover the beaker, and heat gently until vigorous reaction ceases. Remove the cover, evaporate the solution to 5-10 ml, cool, and add 3-4 ml of concentrated hydrochloric acid. Dilute the solution to approximately 75 ml with water, add 1-2 drops of 0.1% methyl red solution, and precipitate the aluminum as described in the procedure. Add a small amount of paper pulp, boil the solution for 30 seconds to coagulate the precipitate, filter the solution and wash the precipitate as described. Combine the paper containing the residual aluminum with that containing the initial precipitate, then proceed as described. Reserve the filtrate and washings for the determination of calcium and magnesium (Note 15).

17. To ensure the recovery of any of the aluminum precipitate that may have adhered to the beaker, funnel, and stirring rod during the filtration step, wipe the rod and the top inner parts of the beaker and funnel with small moistened pieces of filter paper, and add the paper to the platinum crucible containing the aluminum precipitate.

18. If the precipitate is ignited at temperatures below 1200°C, the resulting aluminum oxide is hygroscopic[1].

19. If the sample contains phosphate, most or all of the phosphorus will be present as phosphorus pentoxide (P_2O_5) in the ignited aluminum oxide residue. The phosphorus pentoxide content of the residue should be determined spectrophotometrically, by the Phosphovanadomolybdic Acid Method (p 87), after fusion of the residue with sodium carbonate, and the amount obtained should be subtracted from the weight of the aluminum oxide residue.

20. Aluminum can be determined in refractory silicate rocks and minerals by the method described in Procedure C, but this procedure is directly applicable to samples containing fluoride (cf., Procedure C, Note 25).

21. Ignition of the sample oxidizes any reducing substances (e.g., carbonaceous material and pyrite) which could attack the platinum crucible during the subsequent fusion procedure.

22. If the sample contains an appreciable amount of iron, the mixed hydrous oxide (R_2O_3) precipitate, first obtained by neutralizing the solution

with ammonium hydroxide, should be allowed to settle after the solution is heated to the boiling point. The colour of the indicator will then be perceptible in the supernatant solution. This facilitates the final endpoint adjustment (Note 10)[1].

23. It is not necessary to transfer the precipitate quantitatively to the filter paper at this stage.

24. Complete removal of the hydrous oxide of aluminum from filter paper, by treatment with acid, is difficult. Consequently, to avoid loss of aluminum, both the precipitate and paper should be decomposed by treatment with acids[1].

25. If the sample contains, or is suspected to contain fluoride, add 25 ml of 50% sulphuric acid at this stage, and evaporate the solution to approximately 10 ml. Cool, wash down the sides of the beaker with water, evaporate the solution to fumes of sulphur trioxide, then repeat the washing and evaporation steps two more times to ensure the complete removal of fluoride ion. Evaporate the solution to approximately 5 ml or until the sodium salts begin to crystallize, then proceed as described (Note 3). If fluoride is not completely removed, the result obtained for aluminum will be inaccurate because it is not completely precipitated as the hydrous oxide in the presence of fluoride ion[5]. In addition, depending on the amount of fluoride ion present, calcium will be partly precipitated as the insoluble fluoride (CaF_2) during the subsequent and final ammonium hydroxide separation procedures, and will contaminate both the mixed hydrous oxide (R_2O_3) precipitate and the final aluminum hydrous oxide precipitate. This also causes low results for calcium if it is to be determined in the filtrate remaining after the ammonium hydroxide separation procedure (Note 15)[5,7].

26. In procedures in which silica has been separated after dehydration with acids, the aluminum hydrous oxide precipitate is usually contaminated with a small amount of occluded silica. In exact work, the occluded silica is removed from the ignited aluminum oxide residue by volatilization as silicon tetrafluoride with hydrofluoric and sulphuric acids, followed by the removal of the excess sulphuric acid by evaporation to dryness, and re-ignition and weighing of the residue[1]. Some phosphate will also be volatilized as phosphoric acid if the evaporation of the excess sulphuric acid is conducted at a high temperature[9].

27. Alternatively, aluminum can be determined in carbonate rocks containing fluoride by the method described in Procedure A. However, if the sample contains an appreciable amount of calcium (e.g., limestone), some difficulty may be experienced in obtaining complete dissolution of the calcium sulphate salts unless a small sample is taken for analysis.

28. If the sample contains approximately 10 mg or less of aluminum, the aluminum can be determined, after the cupferron-chloroform separation procedure, by precipitation with 8-hydroxyquinoline as described in the Gravimetric-8-Hydroxyquinoline Method for aluminum (p 151).

Calculations

$$\%Al_2O_3 = \frac{W_{Al} - W_P - W_B}{\text{Sample weight (g)}} \times 100$$

where:

W_{Al} = weight (g) of the ignited aluminum oxide residue.

W_P = weight (g) of phosphorus pentoxide (P_2O_5) found in the residue.

W_B = weight (g) of the ignited blank residue.

Other applications

The methods described in Procedures A and C can be employed to determine aluminum in fire-brick and glass. The method described in Procedure C is applicable to bauxite and magnesite[10], and that in Procedure D is applicable to cement.

References

1. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 77-78, 494-505 (1953).

2. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 4, pp 387-388, 398-400 (1966).

3. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 136-142, 345-348 (1968).

4. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, 57 (1938).

5. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 738, 869 (1953).

6. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 737-738 (1948).

7. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 621-622 (1953).

8. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 4, 377 (1966).

9. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 675 (1953).

10. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D.Van Nostrand Company, Inc., New York, vol. 1, pp 68-69, 592-593 (1962).

DETERMINATION OF ALUMINUM IN IRON, CHROMIUM, TITANIUM, MOLYBDENUM AND SULPHIDE ORES AND MILL PRODUCTS BY PRECIPITATION WITH 8-HYDROXYQUINOLINE

Principle

Aluminum is determined by weighing as the 8-hydroxyquinolate [$Al(C_9H_6NO)_3$] after precipitation with 8-hydroxyquinoline from a weakly acid (pH 5.5) tartaric-acetic acid medium[1,2].

Outline

Iron, chromium and sulphide ores and mill products are decomposed with hydrochloric and nitric acids. Arsenic, antimony, and tin are removed by volatilization as the bromides from a perchloric acid medium, and the solution is evaporated to fumes of perchloric acid to dehydrate silica and to oxidize chromium to the hexavalent state. The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate, and the melt is dissolved in the initial filtrate. Iron, chromium, and various other elements (copper, cobalt, cadmium, nickel, zinc, lead, and bismuth) are separated from aluminum by electrolysis with a mercury cathode, and fluoride, if present, is removed from the resultant electrolyte by evaporation with sulphuric acid. Aluminum and various other elements (zirconium and titanium) are subsequently precipitated as the hydrous oxides with ammonium hydroxide, and separated from calcium, magnesium, and manganese by filtration. The mixed hydrous oxide (R_2O_3) precipitate is dissolved in dilute hydrochloric acid, and the hydrous oxides are re-precipitated to remove occluded elements (calcium, magnesium, and manganese). After dissolution of the precipitate, titanium, zirconium, and various other co-precipitated or occluded elements (vanadium and molybdenum) are separated from aluminum by chloroform extraction of their cupferron complexes. The aluminum in the resulting aqueous phase is ultimately precipitated with 8-hydroxyquinoline, and the precipitate is separated by filtration, dried, and weighed.

Titanium and molybdenum ores and mill products are decomposed with hydrochloric, nitric, and hydrofluoric acids. Arsenic and antimony are removed by volatilization as the bromides from a sulphuric acid medium, and the solution is evaporated to fumes of sulphur trioxide to remove silica and excess hydrofluoric acid. The acid-insoluble material is removed by filtration, ignited, and fused with sodium carbonate. The melt is dissolved in the initial filtrate and iron, titanium, molybdenum, and various other elements (zirconium and vanadium) are ultimately separated from aluminum by chloroform extraction of their cupferron complexes.

If manganese, chromium, bismuth, copper, cobalt, cadmium, nickel, zinc, and appreciable amounts of calcium and magnesium are absent, the aluminum in the resulting aqueous phase is ultimately precipitated with 8-hydroxyquinoline and determined as described above.

If the above elements are present, aluminum is precipitated twice as the hydrous oxide with ammonium hydroxide and separated from calcium, magnesium, manganese, and chromium, and from most of the copper, cobalt, cadmium, nickel, and zinc by filtration. After dissolution of the precipitate, bismuth and the occluded elements are separated from aluminum by electrolysis with a mercury cathode. The aluminum in the resulting electrolyte is ultimately precipitated with 8-hydroxyquinoline.

Discussion of interferences

Numerous elements interfere in the determination of aluminum by precipitation as the 8-hydroxyquinolate because they form insoluble hydroxyquinolate compounds [e.g., copper (II), cobalt, nickel, cadmium, zinc, manganese, iron (II), iron (III), chromium (III), lead, bismuth, antimony (III), antimony (V), titanium, zirconium, vanadium (IV), vanadium (V), molybdenum (VI), tungsten (VI), gallium, indium, thallium (III), silver, palladium (II), ruthenium (III), mercury (I), mercury (II), uranium, and thorium][3,4], or because they are occluded, if present in large amounts (e.g., calcium and magnesium), by the precipitate[5]. Large amounts of phosphate interfere because of the formation of aluminum phosphate, but small amounts may be present during the precipitation of aluminum without causing appreciable error in the aluminum result[5-7]. Fluoride prevents the complete precipitation of aluminum with 8-hydroxyquinoline because it forms a stable fluo complex with aluminum[8].

Fluoride, if present in the sample, or hydrofluoric acid employed for sample decomposition, are removed by repeated evaporation of the sample solution with sulphuric acid. Co-precipitation of antimony is avoided by volatilizing it (and also arsenic, tin, and rhenium) as the bromide from a hydrobromic-perchloric or a hydrobromic-sulphuric acid medium. Interference from copper, cobalt, nickel, cadmium, zinc, iron, chromium, lead, bismuth, gallium, indium, thallium, silver, palladium, mercury, and ruthenium is eliminated by separating these elements, and various other elements that may be present (tin, germanium, rhodium, iridium, platinum, and gold) by electrolysis with a mercury cathode in a dilute perchloric or sulphuric acid medium[9]. Interference from manganese and large amounts of calcium and magnesium is avoided by separating aluminum from these elements, and from chromium (VI) by precipitation as the hydrous oxide with ammonium hydroxide from an ammonium chloride medium. Co-precipitation of titanium, zirconium, vanadium, and molybdenum is prevented by separating these elements (and some niobium and tantalum, if present) from aluminum by chloroform extraction of their cupferron complexes from a 10% sulphuric acid medium[10].

Precipitation of aluminum with 8-hydroxyquinoline in the presence of tartaric acid prevents its precipitation as the hydrous oxide during the initial partial neutralization of the solution with ammonium hydroxide, and eliminates possible error resulting from the formation of basic aluminum acetate[6,8].

Tungsten (more than approximately 5 mg), uranium, thorium and, possibly niobium and tantalum interfere in this method[2,4]. Beryllium does not interfere because it does not react with 8-hydroxyquinoline in acid media[3,8].

Range

The method is suitable for iron, chromium and sulphide ores and mill products containing approximately 0.05 to 10% of aluminum, and for titanium and molybdenum ores and mill products containing approximately 0.1 to 10% of aluminum.

Apparatus

Mercury cathode.

Reagents

8-Hydroxyquinoline solution, 2.5% w/v. Dissolve 25 g of the reagent (Oxine) in 60 ml of glacial acetic acid and, while stirring, add approximately 200 ml of water. If necessary, filter and dilute the solution to 1 litre with water.

Iron solution, 1% w/v. Dissolve 1 g of high-purity iron metal (aluminum-free) in 10 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, and dilute the solution to 100 ml with water.

Cupferron solution, 9% w/v. Prepare fresh as required, and filter the solution, if necessary.

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Tartaric acid solution, 2% w/v.

Ammonium hydroxide, 50% and 20% v/v.

Sulphuric acid, 50% and 5% v/v.

Hydrochloric acid, 50%, 5%, and 2% v/v.

Ammonium chloride wash solution, 2% w/v. Dissolve 20 g of the reagent in approximately 300 ml of water, add 3 drops of concentrated ammonium hydroxide, and dilute to 1 litre with water.

Chloroform. Analytical reagent-grade.

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Iron, chromium and sulphide ores and mill products

Transfer 1 g of powdered sample (Notes 1 and 2) to a 400-ml beaker, moisten with several ml of water, and add 20 ml of concentrated hydrochloric acid. Cover the beaker, and heat gently until the decomposition of acid-soluble material is complete. Add 5 ml of concentrated nitric acid, heat gently for approximately 5 minutes, then add 10 ml of concentrated hydrobromic acid and 20 ml of concentrated perchloric acid, boil for several minutes, remove the cover, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, add 10 ml of concentrated hydrobromic acid, and evaporate the solution to fumes of perchloric acid again (Note 3). Cover the beaker, and continue fuming for 10-15 minutes to dehydrate the silica and to oxidize chromium, if present, to the hexavalent state. Cool, remove the cover, add 50 ml of water and, if necessary, several crystals of sodium nitrite to reduce any manganese dioxide present. Heat gently to dissolve the soluble salts, and filter the solution (Whatman No. 541 paper) into a 400-ml beaker. Transfer the acid-insoluble residue quantitatively to the filter paper, wash the paper and residue 3-4 times with hot water, then 3-4 times with hot 2% hydrochloric acid, and 6-8 times with hot water or until the washings are no longer acidic (Note 4).

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 800°C. Cool the crucible, add 1 ml of 50% sulphuric acid and 5-10 ml of concentrated hydrofluoric acid, heat gently to decompose the residue, then evaporate the solution to dryness. Fuse the residue with 1-2 g of sodium carbonate, cool, and transfer the crucible and contents to the beaker (covered) containing the initial filtrate. When dissolution of the melt is complete, remove the crucible after washing it thoroughly with hot water, and evaporate the solution to fumes of perchloric acid to remove hydrochloric acid. Wash down the sides of the beaker with water, evaporate the solution to approximately 8 ml (Note 5), then add 50 ml of water and heat gently until the solution is clear (Note 6).

Cool the solution to room temperature (Note 7), transfer it to a mercury cathode cell, dilute to about 275 ml with water, and electrolyze for 1 hour at approximately 10 amperes. Filter the electrolyte (Whatman No. 541 paper) into the 400-ml beaker that contained the initial filtrate, and wash the paper thoroughly with hot 2% hydrochloric acid and hot water. Discard the paper.

Evaporate the resulting solution to approximately 180 ml (Note 8), and add 10 ml of concentrated hydrochloric acid (Note 9) and several drops of 0.1% methyl red solution. Neutralize the solution approximately with concentrated ammonium hydroxide (Note 10), and add several drops in excess. Heat the solution to the boiling point (Note 11), add 50% hydrochloric acid, by drops, until the colour of the solution changes to a faint pink, then add 20% ammonium hydroxide, by drops, until the colour changes to a distinct canary yellow (Note 12). Boil the solution for approximately 30 seconds to coagulate the resulting mixed hydrous oxide precipitate, allow the precipitate to settle for about 1 minute, then, without delay (Note 13), filter the solution (Whatman No. 541 paper) into an 800-ml beaker, and wash the beaker, paper, and precipitate 4 or 5 times with hot 2% ammonium chloride solution (Note 14).

Using a jet of hot water, carefully transfer the precipitate to the beaker in which the precipitation was carried out, add 7 ml of concentrated hydrochloric acid, and heat gently to dissolve the precipitate. Dilute the solution to approximately 150 ml with water, and re-precipitate the mixed hydrous oxides as described above. Filter the solution through the same filter paper (Note 15), wash the paper and precipitate 8 times with hot 2% ammonium chloride solution, and collect the filtrate and washings in the beaker containing the initial filtrate (Note 16).

Transfer the paper and precipitate (Note 17) to the beaker in which the precipitation was carried out, place the beaker under the funnel and wash the funnel with hot 5% hydrochloric acid. Add 40 ml of 50% sulphuric acid and 10 ml each of concentrated nitric and hydrochloric acids, and macerate the paper with a stirring rod. Cover the beaker, and boil the solution for 20-30 minutes to decompose the paper. Cool, remove the cover, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with a small amount of water, and add 10 ml each of concentrated nitric and hydrochloric acids. Evaporate the solution to fumes again, and continue the nitric-hydrochloric acid treatment and the subsequent evaporation to fumes until the filter paper has been completely destroyed and the yellow colour due to carbonaceous material has disappeared. Evaporate the solution to approximately 8 ml, cool, add 30 ml of water and, if necessary, heat gently to clarify the solution.

Transfer the resulting solution to a 125-ml separatory funnel, dilute to approximately 80 ml with water, and cool to about 10°C in an ice-bath. Add sufficient cold 9% cupferron solution (Note 18) to precipitate titanium, zirconium, vanadium, and iron (if present), mix, stopper, and extract the cupferrates by repeated shaking, for 1 minute each time, with two 15-ml and then three or more 5-ml portions of chloroform until the organic layer is colourless. Discard each extract. Transfer the aqueous phase to a 400-ml beaker, warm gently to remove residual chloroform, then evaporate the solution to approximately 50 ml. Cover the beaker, add 10 ml each of concentrated nitric and hydrochloric acids, and boil the solution for 20-30 minutes to destroy organic material. Cool, remove the cover, and evaporate the solution to fumes of sulphur trioxide. If organic material is still present, repeat the treatment with nitric and hydrochloric acids, then evaporate the solution to approximately 5 ml (Notes 5 and 19). Cool, add 50 ml of water and heat gently to dissolve the salts.

If the sample contains 10 mg (i.e., 1%) or less of aluminum, filter the solution (Whatman No. 541 paper) into a 600-ml beaker to ensure the removal of any residual silica that may be present. Wash the paper and residue 5 times with hot 2% hydrochloric acid, then 5 times with hot water, and discard the paper.

If the sample contains more than 10 mg of aluminum, filter the solution into a 200-ml volumetric flask, wash the paper and residue as described above, dilute the filtrate to volume with water and mix.

Add 5 ml each of concentrated hydrochloric acid and 2% tartaric acid solution to the initial sample solution, or to a 20- 100-ml aliquot (in a 600-ml beaker) containing up to 10 mg of aluminum, and dilute the solution to approximately 200 ml with water. Add several drops of 0.1% methyl red solution, and carefully add 50% ammonium hydroxide until the colour of the indicator just changes. Add sufficient 2.5% 8-hydroxyquinoline solution to precipitate the aluminum and to provide a suitable excess (Notes 20 and 21), then, using a pH meter, adjust the pH of the solution to 5.5 ± 0.05 with 50% ammonium hydroxide. Maintain the resulting solution at 70°C for 20 minutes, allow it to stand for at least 10 minutes at room temperature, then, using suction, filter the solution through a tared, sintered-glass, medium-porosity filtering crucible. Transfer the precipitate quantitatively to the crucible, and wash it 6-8 times with approximately 8-ml portions of warm water (Notes 22 and 23). Dry the precipitate for 1.5 hours at 135°C, cool in a dessicator and weigh. Repeat the drying and weighing until constant weight is obtained, and correct the result obtained for the sample by subtracting that obtained for the reagent blank.

B - Titanium and molybdenum ores and mill products

Transfer 0.5 g of powdered sample to a 400-ml Teflon beaker, moisten with several ml of water, and add 10 ml each of concentrated hydrochloric, nitric, and hydrofluoric acids. Cover the beaker with a Teflon cover, and heat gently until the decomposition of acid-soluble material is complete. Add 10 ml of concentrated hydrobromic acid and 50 ml of 50% sulphuric acid, boil for several minutes, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, add 10 ml of concentrated hydrobromic acid, and evaporate the solution to fumes of sulphur trioxide again (Note 24). Cool, wash down the sides of the beaker with water, evaporate the solution to fumes, then repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid. Cool, add approximately 50 ml of water, heat gently to dissolve the soluble salts, and filter the solution (Whatman No. 541 paper) into a 400-ml pyrex beaker. Transfer the acid-insoluble residue quantitatively to the filter paper, and wash the paper and residue 3-4 times with hot 5% sulphuric acid and 3-4 times with hot water.

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 800°C. Fuse the residue with 2-3 g of sodium carbonate, cool, and transfer the crucible and contents to the beaker (covered) containing the initial filtrate. When dissolution of the melt is complete, remove the crucible after washing it thoroughly with hot water, and evaporate the resulting solution to fumes of sulphur trioxide. Cover the beaker, and fume for about 5 minutes to dehydrate any silica present, then remove the cover and evaporate the solution to approximately 15 ml. Cool, carefully add 75 ml of water, cool the solution to room temperature, filter it (Whatman No. 541 paper) into a 500-ml separatory funnel, and wash the paper and residue 4 or 5 times with 5% sulphuric acid. Discard the paper and residue.

Dilute the filtrate to approximately 150 ml with water, cool the solution to about 10°C in an ice-bath, then precipitate and extract the iron and the titanium or molybdenum cupferrates, as described above, using two 50-ml and then three or more 25-ml portions of chloroform until the organic layer is colourless. Transfer the aqueous layer to a 400-ml beaker, warm gently to remove residual chloroform, and evaporate the solution to approximately 50 ml. Decompose the organic material with hydrochloric and nitric acids as described above (Note 25), and evaporate the solution to approximately 5 ml (Note 5). Cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid, and heat gently to dissolve the salts (Note 26).

Dilute the resulting solution to approximately 200 ml with water (Note 9), add several drops of 0.1% methyl red solution, and precipitate the hydrous oxide of aluminum twice with ammonium hydroxide as described in Procedure A. Transfer the paper and precipitate to the beaker in which the precipitation was carried out, place the beaker under the funnel, and wash the funnel with hot 5% hydrochloric acid. Add 40 ml of 50% sulphuric acid, then decompose the paper, as described in Procedure A, by repeated treatment with hydrochloric and nitric acids. When the yellow colour due to the carbonaceous material has completely disappeared, evaporate the solution to approximately 6 ml, cool, add 50 ml of water and heat gently to clarify the solution (Note 27).

Cool the solution to room temperature, transfer it to a mercury cathode cell, dilute to approximately 200 ml with water, and electrolyze the solution and filter the electrolyte as described in Procedure A. Evaporate the resulting solution to approximately 30 ml, add 10 ml of concentrated hydrobromic acid to volatilize any residual mercury salts, and evaporate the solution to fumes of sulphur trioxide. Cool, add 50 ml of water and heat gently to dissolve the salts.

If the sample contains 10 mg or less of aluminum, filter the solution into a 600-ml beaker, and proceed with the precipitation of aluminum 8-hydroxyquinolate and the subsequent treatment of the precipitate as described above.

If the sample contains more than 10 mg of aluminum, filter the solution into a 100-ml volumetric flask, and dilute to volume with water. Transfer a 10-50-ml aliquot, containing up to 10 mg of aluminum, to a 600-ml beaker, and proceed with the precipitation and subsequent determination of aluminum as described above.

Notes

1. This procedure is not applicable to tungsten ores and mill products, and is probably not applicable to manganese ores and concentrates.

2. If the sample contains fluoride, an appreciable amount of calcium, and only a small amount of silica, approximately 10-20 mg of pure powdered silica should be added at this stage so that most of the fluoride will be volatilized as silicon tetrafluoride during the decomposition procedure (Note 8)[11].

3. If the sample contains an appreciable amount of antimony, arsenic or tin, repeated treatment of the solution with hydrobromic acid, followed by evaporation to fumes of perchloric acid, is recommended to ensure the complete removal of these elements.

4. If the sample contains lead or silver, the initial washing of the acid-insoluble residue with hot water prevents the residue from becoming contaminated with insoluble lead and silver chlorides. Deflagration may occur during the subsequent ignition if the residue is not washed free of perchlorates.

5. The sample solution should not be allowed to evaporate to dryness. This results in the formation of anhydrous aluminum compounds, which are virtually insoluble in water or dilute acid, and causes low results for aluminum[12].

6. Any residual silica (or possibly lead sulphate) that is present at this stage may be ignored because it is removed during filtration of the electrolyte, after the subsequent mercury cathode separation.

7. If the sample is an iron ore or concentrate, the major portion of the iron can be separated at this stage (instead of by the mercury cathode separation) by methyl isobutyl ketone (or ethyl or isopropyl ether) extraction of its chloro complex from a 7.3 M hydrochloric acid medium, as follows[1]:

Add 30 ml of 63% hydrochloric acid, and transfer the resulting solution to a 250-ml separatory funnel. Wash the beaker with 20 ml of the same solution, and add the washings to the funnel. Add 60 ml of methyl isobutyl ketone, stopper, shake for approximately 1 minute, and allow the mixture to stand until the layers separate. Drain the lower aqueous layer into the 400-ml beaker that contained the initial solution, and wash the ketone layer three times, by shaking for 1 minute each time with a 5-ml portion of 63% hydrochloric acid. Add the washings to the initial aqueous phase, heat the solution gently to remove the residual methyl isobutyl ketone, then add 5 ml of concentrated nitric acid, and evaporate (Note 8) the solution to fumes of perchloric acid. Cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid, and heat to dissolve the salts. If necessary, filter the solution (Whatman No. 541 paper) into a 400-ml beaker to remove residual silica, wash the beaker, paper, and residue with hot 2% hydrochloric acid and hot water, and discard the paper and residue. Dilute the solution to 200 ml with water, then proceed as described with the ammonium hydroxide separation procedure.

8. Fluoride, particularly in the presence of an appreciable amount of calcium (Note 2), is difficult to remove completely by evaporation with perchloric acid[13]. Consequently, if the sample contains, or is suspected to contain fluoride, add 15 ml of 50% sulphuric acid at this stage and evaporate the solution to 5-6 ml. Cool, wash down the sides of the beaker with water, evaporate the solution to fumes of sulphur trioxide, then repeat the washing and evaporation steps two more times to ensure the complete removal of fluoride ion (Note 5). Cool, add 50 ml of water and 10 ml of concentrated hydrochloric acid, heat gently to dissolve the salts, dilute the solution to approximately 180 ml with water, then proceed as described. If fluoride is not completely removed, prior to the ammonium hydroxide separation, the result obtained for aluminum will be low because it is not completely precipitated as the hydrous oxide in the presence of fluoride ion[13]. In addition, depending on the amount of fluoride ion present, calcium will be partly precipited as the insoluble fluoride (CaF_2) during the subsequent ammonium hydroxide separation procedure. This also causes low results for calcium if it is to be determined in the filtrate remaining after the ammonium hydroxide separation procedure (Note 16)[11].

9. If calcium and magnesium are to be determined in the filtrate remaining after the separation of aluminum and other elements by precipitation with ammonium hydroxide (Note 16), some iron (III) solution should be added at this stage as a collector for phosphate if the sample contains phosphate in amounts approximately equal to, or in excess of that required to combine stoichiometrically with the aluminum present [i.e., 1 mg of aluminum = 2.63 mg of phosphorus pentoxide (P_2O_5)]. If iron is not added under these conditions, low results will be obtained for calcium and magnesium because of their partial precipitation as insoluble phosphates during the ammonium hydroxide separation procedure. Approximately a tenfold excess of iron (III) (i.e., 1 ml of a 1% solution) should be added for every mg of excess phosphate (as phosphorus pentoxide) present[11]. The addition of 1 ml of 1% iron (III) solution is also recommended as a collector for aluminum, if the amount present is expected to be 2-3 mg or less. The iron that is added does not interfere in the final determination of aluminum because it is removed during the subsequent cupferron-chloroform extraction step.

10. If calcium and/or magnesium are to be determined in the filtrate remaining after the ammonium hydroxide separation of aluminum and other elements (Note 16), carbonate-free ammonium hydroxide should be employed for neutralization and precipitation to avoid loss of calcium and magnesium resulting from their co-precipitation as insoluble carbonates[11]. If a carbonate-free commercial product is not available, a pure solution (approximately 15 M) can be prepared by saturating freshly boiled and cooled distilled water with ammonia gas.

11. If the sample solution contains iron (Note 9), the mixed hydrous oxide (R_2O_3) precipitate obtained by neutralizing the solution with ammonium hydroxide should be allowed to settle after the solution is heated to the boiling point. The colour of the indicator will then be perceptible in the supernatant solution. This facilitates the final end-point adjustment (Note 12)[10].

12. Particular care must be taken in adjusting the end-point. The precipitation of aluminum is incomplete if insufficient ammonium hydroxide is employed, and an excess results in loss of aluminum because of the partial redissolution of the precipitate[10]. The use of dilute hydrochloric acid, before the final adjustment of the end-point, makes the colour change, in the presence of the precipitate, easier to observe. If the colour of the solution changes to orange, during or after the subsequent boiling stage to coagulate the precipitate, the end-point should be re-adjusted with 20% ammonium hydroxide.

13. The time-lapse between the precipitation and filtration should be kept to a minimum to avoid air-oxidation and subsequent co-precipitation of manganese as the dioxide[1].

14. Hot water should not be used to wash the precipitate. This results in loss of aluminum because of the conversion (i.e., peptization) of the hydrous oxide to the colloidal state[10].

15. It is not necessary to transfer the precipitate quantitatively to the filter paper at this stage.

16. The combined filtrates and washings can be used for the determination of calcium and magnesium by the Volumetric-Oxalate (p 243) and the Gravimetric-Pyrophosphate (p 182) Methods, respectively.

17. Complete removal of the hydrous oxide of aluminum from filter paper, by treatment with acid, is difficult. Consequently, to avoid loss of aluminum, both the precipitate and paper should be decomposed by treatment with acids[10].

18. Approximately 2-2.5 ml of 9% cupferron solution are usually sufficient for the complexation of 10 mg of metal ion. To test for completeness of precipitation, extract the solution twice with chloroform, then add 1-2 ml of cupferron solution. Complete precipitation is indicated by a transient white precipitate resulting from the presence of excess cupferron.

19. If the organic material has been completely destroyed the solution should be water-white.

20. Theoretically 1 mg of aluminum combines with 16.14 mg of 8-hydroxyquinoline (i.e., 0.65 ml of a 2.5% solution). However, 1-1.5 ml of a 2.5% solution should be added for every mg of aluminum present, and at least 10 ml should be added if the solution contains 7 mg or less[2]. Sufficient reagent has been added to precipitate the aluminum if the supernatant solution is yellow after the subsequent pH adjustment. Because 8-hydroxyquinoline is only slightly soluble in aqueous media, the addition of excessive amounts of the reagent solution should be avoided. This may cause high results for aluminum because the excess reagent will coprecipitate, to a certain extent, with the aluminum, and may not be completely removed from the precipitate by volatilization at the drying temperature (135°C) employed[1].

21. The same amount of 8-hydroxyquinoline solution that has been added to the sample solution should be added to the reagent blank solution.

22. The total amount of water used to wash the precipitate should not exceed approximately 60 ml. Excessive washing may result in loss of aluminum.

23. Aluminum can be determined volumetrically at this stage, after dissolution of the precipitate in dilute hydrochloric acid, by bromination of the 8-hydroxyquinoline with a slight excess of standard potassium bromate-bromide solution, followed by the addition of potassium iodide and titration of the liberated iodine with standard sodium thiosulphate solution[1,3,8]. However, because the same care is required in the filtration of the precipitate as in the gravimetric determination, the only advantage inherent in the volumetric determination is the time that is saved by the elimination of the drying operation. Both the volumetric and the gravimetric methods generally yield slightly high results for aluminum because of the occlusion of small amounts of 8-hydroxyquinoline by the aluminum precipitate[3,5,8].

24. If the sample contains an appreciable amount of antimony or arsenic, repeated treatment of the solution with hydrobromic acid, followed by evaporation to fumes of sulphur trioxide, is recommended to ensure the complete removal of these elements.

25. If the sample contains chromium, add 5 ml of concentrated perchloric acid, during or after the destruction of the organic material, to oxidize chromium to the hexavalent state. Chromium will be separated from aluminum during the subsequent ammonium hydroxide separation step, because chromium (VI) is not precipitated as the hydrous oxide with ammonium hydroxide[10].

26. If manganese, chromium,bismuth, copper, nickel, cadmium, zinc, cobalt, and appreciable amounts of calcium and magnesium are absent, and if calcium and magnesium determinations are not required, omit the subsequent ammonium hydroxide and mercury cathode separations, and proceed with the precipitation and weighing of aluminum 8-hydroxyquinolate as described in the subsequent procedure.

27. If iron was not added to coprecipitate phosphate and/or small amounts of aluminum (Note 9), and the sample does not contain bismuth or large amounts of other elements (e.g., Note 26), omit the subsequent mercury cathode separation and proceed with the precipitation and weighing of aluminum 8-hydroxyquinolate as described in the subsequent procedure.

Calculations

$$\%Al_2O_3 = \frac{0.1110 \times (W_{Al} - W_B)}{S} \times 100$$

where:

W_{Al} = weight (g) of the dried aluminum 8-hydroxyquinoline precipitate.

W_B = weight (g) of the dried blank.

S = weight (g) of the sample in the solution or aliquot taken for analysis.

$\%Al = 0.5292 \times \%Al_2O_3$

Other applications

The method described in Procedure A can be employed to determine aluminum in iron, steel, and copper, chromium, nickel, and zinc metals. The method described in Procedure B is applicable to titanium, vanadium, and molybdenum metals[2].

References

1. Technical Committee 102 - Iron Ores, "Determination of Aluminum Content", International Organization for Standardization, Document 111E, October (1970).
2. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E120-69, pp 555-558 (1971).
3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 122-124, 507-510 (1953).
4. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 179-183 (1959).
5. C.C. Miller and R.A. Chalmers, Analyst, 78, 686 (1953).
6. L. Kampf, Ind. Eng. Chem., Anal. Ed., 13, 72 (1941).
7. R.A. Hummel and E.B. Sandell, Anal. Chim. Acta, 7, 308 (1952).
8. H.B. Knowles, J. Res. Natl. Bur. Std., 15, 87 (1935).
9. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 94-95 (1938).
10. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 494-505 (1953).
11. Idem, ibid., 622 (1953).
12. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 4, 377 (1966).
13. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 858 (1953).

DETERMINATION OF CARBON DIOXIDE OR "CARBONATE" CARBON IN ORES AND MILL PRODUCTS, SILICATE AND CARBONATE ROCKS AND MINERALS, SANDSTONE, SILICA SAND, CLAY, AND SHALE BY THE EVOLUTION METHOD

Principle

This method[1-4] is based on the liberation of carbon dioxide from carbonate-bearing material by acid treatment in a carbon dioxide-free air atmosphere. The liberated gas is purified, dried, and subsequently collected in a weighed absorption bulb containing Ascarite (asbestos impregnated with sodium hydroxide) and anhydrous magnesium perchlorate, which absorb the carbon dioxide and the water formed during the reaction of the gas with sodium hydroxide, respectively. Carbon dioxide is determined from the increase in weight of the absorption bulb. The corresponding reactions for these processes are:

$$CO_3^{=} + 2H^+ \rightarrow CO_2\uparrow + H_2O$$

$$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O.$$

Outline

The sample is treated with dilute perchloric acid in a carbon dioxide-free atmosphere, and the solution is boiled to expel the resultant carbon dioxide. The liberated gas is passed through a condenser and a purification train to remove water vapour, various gases, and volatile constituents. The purified carbon dioxide is collected in a weighed absorption bulb and the bulb is re-weighed.

Discussion of interferences

Sulphur dioxide, hydrogen sulphide, arsine, chlorine, and other volatile compounds (e.g., hydrochloric acid), that may be produced or evolved by the reaction of perchloric acid with various sample components (e.g., chlorides, and pyrite, arsenopyrite and other sulphur compounds), are absorbed by Ascarite and will cause inaccurate results for carbon dioxide or "carbonate" carbon if they are not removed from the evolved gas phase, prior to the collection of the liberated carbon dioxide in the weighed absorption bulb. Water vapour interferes because it is absorbed by anhydrous magnesium perchlorate[1-4].

Most of the water vapour that is formed when the solution is boiled to expel carbon dioxide is removed from the gas stream by the condenser attached to the reaction vessel. The remaining water is removed by passing the gas through two absorption bulbs containing concentrated sulphuric acid and anhydrous magnesium perchlorate. Sulphur dioxide is removed by passing the gas through both hydrogen peroxide and granulated manganese dioxide[1]. Most of the hydrochloric acid and hydrogen sulphide are removed by bubbling the gas through an acidified copper sulphate solution; the remainder are removed by pumice impregnated with anhydrous copper sulphate[1,2,4]. Chlorine is removed by the granulated manganese dioxide[5]. Arsine (AsH_3) is removed both by the copper sulphate solution and by the manganese dioxide[1].

The corresponding reactions for the processes involved in the removal of some of the above gaseous constituents are:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

$$SO_2 + MnO_2 \rightarrow MnSO_4$$

$$2HCl + CuSO_4 \rightarrow CuCl_2 + H_2SO_4$$

$$H_2S + CuSO_4 \rightarrow CuS + H_2SO_4$$

$$2AsH_3 + 3CuSO_4 \rightarrow Cu_3As_2 + 3H_2SO_4$$

$$AsH_3 + 4MnO_2 \rightarrow H_3AsO_4 + 4MnO.$$

A carbon dioxide-guard tube containing Ascarite removes carbon dioxide from the air employed as the carrier gas, and a bulb containing Ascarite and anhydrous magnesium perchlorate protects the weighed absorption bulb and prevents error resulting from the absorption of carbon dioxide and moisture if air is accidentally sucked back during the analysis.

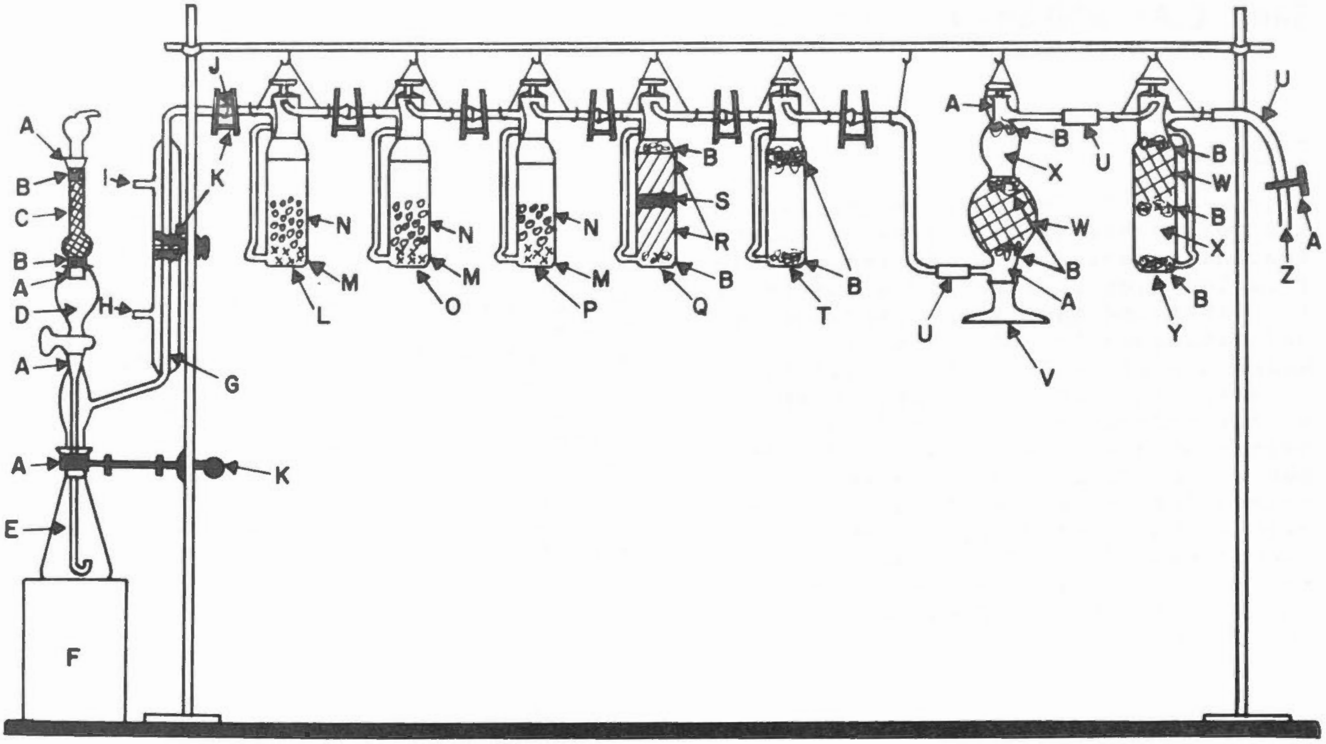

FIGURE 1. Apparatus for the determination of carbon dioxide or "carbonate" carbon

A - Ground-glass joint.
B - Glass-wool.
C - Carbon dioxide-guard tube containing Ascarite (20-30 mesh).
D - Separatory funnel for the addition of acid (approximately 100 ml capacity).
E - Reaction vessel (125-ml Erlenmeyer flask).
F - Heating element.
G - Condenser.
H - Water-inlet.
I - Water-outlet.
J - Ball and socket joint.
K - Clamp.
L - Absorption bulb (Nesbitt-type containing 30% hydrogen peroxide.
M - Pieces of broken glass.
N - Glass beads.
O - Absorption bulb containing 25% copper sulphate solution.
P - Absorption bulb containing concentrated sulphuric acid.
Q - Absorption bulb containing granulated manganese dioxide and pumice impregnated with copper sulphate.
R - Granulated manganese dioxide.
S - Pumice impregnated with copper sulphate.
T - Absorption bulb containing anhydrous magnesium perchlorate (Anhydrone).
U - Rubber tubing.
V - Carbon dioxide-absorption bulb (Fleming-type) containing Ascarite and anhydrous magnesium perchlorate.
W - Ascarite (20-30 mesh).
X - Anhydrous magnesium perchlorate.
Y - Moisture and carbon dioxide-guard absorption bulb containing Ascarite (20-30 mesh) and anhydrous magnesium perchlorate.
Z - Suction tube.
a - Adjustable clamp for regulating suction.

Range

The method is suitable for samples containing more than approximately 0.1% or 0.03% of carbon dioxide or "carbonate" carbon, respectively.

Apparatus

Apparatus for the determination of carbon dioxide or "carbonate" carbon. Illustrated in Figure 1. Leakage in the apparatus is minimized by using ground-glass and ball and socket joint connections wherever possible, and by lubricating these connections and all stopcocks with silicone stopcock grease. The materials used in the purification train should be checked frequently to ensure that their absorbing capacity has not been exhausted.

Reagents

Copper sulphate solution, 25% w/v. Dissolve 62.5 g of anhydrous copper sulphate in approximately 200 ml of 10% sulphuric acid and dilute to 250 ml with the same solution.

Pumice impregnated with copper sulphate. Stir the required amount of granular pumice (10-20 mesh) into an appropriate volume of 25% copper sulphate solution. Allow the mixture to stand for 3-4 hours, remove most of the supernatant solution by decantation, dry the resultant pumice at approximately 130°C, and store in a dry well-stoppered bottle.

Perchloric acid, 25% v/v.

Water (carbon dioxide-free). Freshly boiled and cooled water.

Procedure

In this procedure a blank determination should be carried out before the analysis of the sample (Note 1).

Transfer 0.25-5 g of powdered sample, depending on the expected carbon dioxide content (Note 2), to the reaction vessel (Figure 1), and add sufficient carbon dioxide-free water to cover the lower curved end of the separatory dropping funnel (Note 3). Connect the reaction vessel firmly to the condenser and to the separatory funnel, connect the carbon dioxide-guard tube to the funnel, and start a flow of cold water through the condenser. Connect the suction tube to the bent glass outlet tube from bulb T, open the stopcock in bulb T and in the separatory funnel and, using gentle suction, draw carbon dioxide-free air through the apparatus for approximately 10 minutes to remove any carbon dioxide that may have entered the reaction vessel during the introduction of the sample. Close the stopcock in the funnel and in bulb T, disconnect the suction tube, and connect the weighed carbon dioxide-absorption bulb V (Note 4) and the moisture and carbon dioxide-guard bulb Y to the train, as shown in Figure 1.

Open the stopcocks in bulbs T and Y, and the upper and lower stopcocks in the carbon dioxide-absorption bulb V, then remove the carbon dioxide-guard tube from the separatory funnel. Add 75 ml of 25% perchloric acid to the funnel, replace the guard tube, open the stopcock in the funnel, and allow the acid to flow slowly (Note 5) into the reaction vessel at such a rate that there is a steady evolution of carbon dioxide, corresponding to the passage of approximately 3 bubbles per second, through the absorption bulb L (Note 6). When most of the acid has been added or when effervescence diminishes, connect the suction line to the outlet end of bulb Y. Apply gentle suction (regulated by clamp a), close the stopcock in the separatory funnel, and gradually heat the contents of the reaction vessel to the boiling point (Note 7).

Open the stopcock in the separatory funnel, allow the remainder of the acid to flow slowly into the reaction vessel and regulate the suction so that approximately 2 bubbles of gas per second pass through the train. Continue the gentle boiling of the solution for 5-10 minutes, or until it is judged that all of the carbon dioxide has been expelled from the solution, then gradually reduce the heat, finally remove the source of heat and, by means of suction, increase the flow of air slightly so that a constant slow stream of carbon dioxide-free air is being drawn through the apparatus. Continue to draw air through the apparatus for 10-15 minutes to sweep out all of the carbon dioxide, then disconnect the suction tube, close the upper and lower stopcocks in the carbon dioxide-absorption bulb V, and close the stopcocks in bulbs T and Y and in the separatory funnel. Disconnect the bulb V from the train and place it in the balance case. When the bulb is cool, open the lower stopcock for a moment to equalize the pressure and weigh. Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Notes

1. A blank determination should be made daily or more often if humid conditions prevail. The apparatus should be tested for gas-tightness, prior to the blank determination or the analysis of the sample. In careful work, the apparatus can be tested by determining the carbon dioxide content of pure anhydrous calcium or sodium carbonate. The theoretical amount of carbon dioxide present in the above carbonates is 43.97 and 41.52%, respectively.

2. A 5-g sample should be taken for silicate rocks and minerals, sandstone, silica sand, clay, and shale samples containing approximately 0.5% or less of carbon dioxide; 2-3 g should be taken for samples containing more than approximately 0.5%. From 0.25-1 g may be taken for carbonate rocks and minerals or carbonate-bearing ores and mill products (e.g., limestone, dolomite, calcite, magnesite, cerussite, witherite, strontianite, rhodochrosite, and siderite).

3. The stem of the dropping funnel is bent upwards at its lower end to prevent the escape of carbon dioxide through the tube and should reach nearly to the bottom of the reaction flask.

4. Two weighed carbon dioxide-absorption bulbs can be used in the apparatus if desired. This will ensure the complete absorption of carbon dioxide, and provides an indication when the first bulb must be re-charged. Care must be taken to avoid heat or caustic burns when cleaning out the bulb prior to re-charging. To clean the bulb, soak it for some time in dilute 10% hydrochloric acid, then wash out the solid material thoroughly with water, and dry the bulb in a drying oven before re-charging with Ascarite and anhydrous magnesium perchlorate.

5. With samples containing an appreciable amount of carbonate, the rate of addition of the acid must be slow to prevent too violent an evolution of carbon dioxide. If the sample contains only a small amount of carbonate, the acid can be added relatively rapidly[1,2].

6. If "back-up" of the hydrogen peroxide in bulb L, or of any of the solutions in the subsequent bulbs appears imminent during the addition of the acid, either add the acid more rapidly, or quickly connect the suction line to the outlet end of bulb Y and apply gentle suction.

7. Because some carbonate minerals [e.g., siderite ($FeCO_3$)] release carbon dioxide very slowly when treated with acid at room temperature, the solution should not be heated to the boiling point too rapidly. This may result in too violent an evolution of carbon dioxide, and may cause the solution to be carried over into the absorption bulb containing hydrogen peroxide[4].

Calculations

$$\%\ CO_2 = \frac{I_S - I_B}{\text{Sample weight (g)}} \times 100$$

where:

I_S = increase in weight (g) of the carbon dioxide-absorption bulb for the sample.

I_B = increase in weight (g) of the carbon dioxide-absorption bulb for the blank.

% "Carbonate" C = 0.2729 x % CO_2

References

1. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Mines Branch Monograph 866, Method No. C-1, Part III, April (1958).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 768-770 (1953).

3. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 298-299 (1962).

4. L.C. Peck, "Systematic Analysis of Silicates", U.S. Geol. Surv. Bull., 1170, pp 48-50 (1964).

5. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, 437 (1968).

DETERMINATION OF TOTAL CARBON IN ORES AND MILL PRODUCTS, SILICATE ROCKS AND MINERALS, SANDSTONE, SILICA SAND, CLAY, AND SHALE BY THE DIRECT-COMBUSTION METHOD

Principle

This method is based on the oxidation of carbonaceous material (graphite and organic matter), and the decomposition of inorganic carbonates to carbon dioxide, by combustion of the sample in a water- and carbon dioxide-free oxygen atmosphere. The resultant gas is purified, dried, and subsequently collected in a weighed absorption cartridge containing Ascarite (asbestos impregnated with sodium hydroxide) and anhydrous magnesium perchlorate, which absorb the carbon dioxide and the water formed during the reaction of the gas with sodium hydroxide, respectively. Total carbon is determined indirectly from the increase in weight of the absorption cartridge.

The corresponding reactions for these processes are:

$$C + O_2 \rightarrow CO_2$$

$$2CO_3^{=} \xrightarrow{\text{ignition}} 2CO_2 + O_2$$

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O.$$

Outline

The sample is covered with a mixture of calcium and lead oxides, and ignited at a high temperature in a combustion tube in a water- and carbon dioxide-free oxygen atmosphere. The resulting carbon dioxide is passed through a purification train to remove various gases and water vapour. The purified carbon dioxide is collected in a weighed absorption cartridge and the cartridge is re-weighed.

Discussion of interferences

Chlorine, fluorine, oxides of sulphur, and volatile acid compounds, that may be produced during the combustion of samples containing chloride, fluoride, sulphate, or sulphide compounds, interfere in the determination of total carbon because they are absorbed by Ascarite. Water vapour interferes because it is absorbed by anhydrous magnesium perchlorate[1-3].

Moderate amounts of the above gases and acidic compounds are prevented from volatilizing during combustion by covering the sample with a retentive flux mixture of calcium and lead oxides[4]. Small amounts of excess chlorine and oxides of sulphur that may not be retained by the flux are removed by passing the carbon dioxide through a cartridge containing granulated manganese dioxide[3]. Large amounts of sulphur oxides and acidic sulphur compounds can be removed by bubbling the gas through hydrogen peroxide. Water vapour is removed by passing the gas through a cartridge containing anhydrous magnesium perchlorate. A purification unit containing Ascarite and anhydrous magnesium perchlorate removes carbon dioxide and water, respectively, from the oxygen employed for combustion and as the carrier gas. A bubbler trap containing silicone oil or concentrated sulphuric acid protects the weighed absorption cartridge from atmospheric carbon dioxide and moisture.

Range

The method is suitable for samples containing approximately 0.02 to 10% of carbon but material containing higher concentrations (e.g., carbonate rocks) can be analyzed with reasonable accuracy if smaller samples are taken.

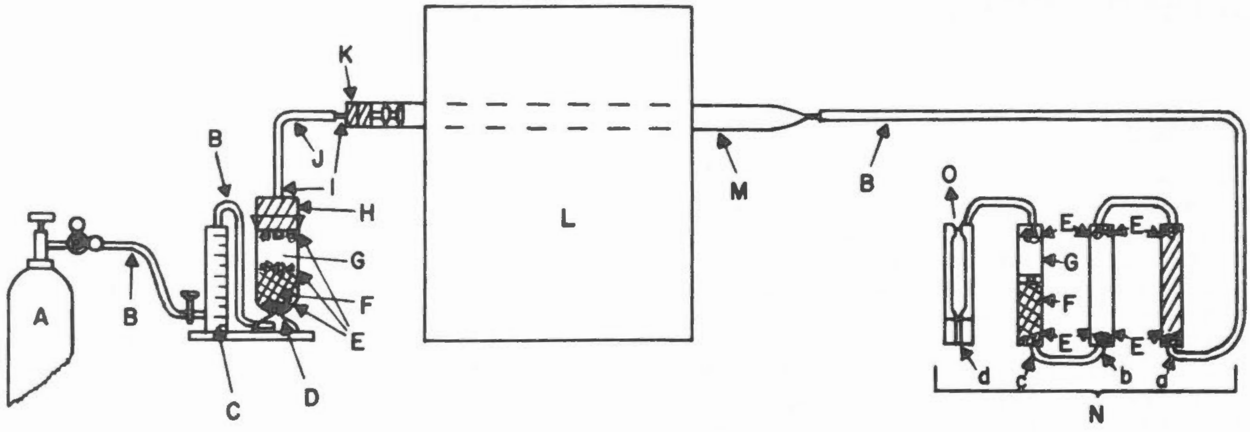

FIGURE 1. Apparatus for the determination of total carbon by direct-combustion

A - Oxygen tank with two-stage regulator.
B - Rubber tubing.
C - Oxygen-flow meter.
D - Purification unit containing Ascarite (20-30 mesh) and anhydrous magnesium perchlorate (Anhydrone).
E - Glass-wool.
F - Ascarite.
G - Anhydrous magnesium perchlorate.
H - Rubber stopper.
I - Glass tube.
J - Tygon tubing (approximately 2.5 ft).
K - Rubber stopper with oxygen (heat-deflector) baffle.
L - Electric furnace, resistance-type with appropriate temperature controls, or induction-type with appropriate power input indicating device.
M - Combustion tube, high-temperature.
N - Purification and carbon dioxide-absorption unit (schematic diagram).
    a - Cartridge containing manganese dioxide.
    b - Cartridge containing anhydrous magnesium perchlorate.
    c - Carbon dioxide-absorption cartridge containing Ascarite and anhydrous magnesium perchlorate.
    d - Bubbler trap containing silicone oil or concentrated sulphuric acid.
O - Oxygen-outlet hole.

Apparatus

Apparatus for the determination of total carbon by direct-combustion. A typical arrangement of the apparatus is illustrated in Figure 1. Various types of apparatus are commercially available but a suitable apparatus can also be readily constructed in the laboratory. The following general recommendations indicate the types of apparatus and related materials that are acceptable[5]:

(a) *Combustion apparatus* - Any apparatus that will heat the sample to the required combustion temperature may be employed. Split-type furnaces with wire-wound heating elements are generally limited to a maximum temperature of 1200°C; resistance furnaces, equipped with non-metallic heating elements, and induction furnaces may be operated at temperatures above 1400°C. If an induction-type furnace is used it must either be equipped with a heated (approximately 300°C) oxidation catalyst tube containing copper oxide to ensure the complete conversion of carbon monoxide to carbon dioxide, or copper oxide can be lightly packed into the exit end of the combustion tube.

(b) *Combustion tubes* - Porcelain, mullite, sillimanite, clay,or quartz tubes that are gas-tight at operating temperatures may be used. Quartz is susceptible to devitrification when used intermittently at temperatures above 1000°C and may become porous. Tubes approximately 30 inches long, with an inside diameter of 1.25 inches, and tapered at one end are generally used with resistance furnaces.

(c) *Combustion boats and covers* - Alundum, clay, or zircon boats and covers may be employed (Note 1). Prior to use the boats and covers should be pre-ignited in air or preferably oxygen, at 1100°C or higher, for at least 15 minutes or until a constant weight is obtained, then cooled, and stored in a dessicator.

(d) *Oxygen-purification unit* - The purity of the oxygen should be not less than 99.5%. It should be passed through two reduction pressure valves (approximately 30 and 2 to 4 psi, respectively) or a suitable two-stage reduction valve to provide a steady and adequate flow. Organic material of any kind is an undesirable impurity. It is usually absent in commercial oxygen, and it generally suffices to remove water and carbon dioxide by passing the gas through anhydrous magnesium perchlorate and Ascarite, respectively. If the presence of carbonaceous matter is suspected, the oxygen should first be passed through a tube that is loosely-packed with copper oxide and heated to about 450°C.

(c) *Carbon dioxide-purification and-absorption unit* - Commercial cartridge-type purification and absorption units (e.g., the Burrell Carbotrane - schematically illustrated in Figure 1) or a unit similar to that shown in the Gravimetric-Evolution Method for carbon dioxide or "carbonate" carbon (p 162,Figure 1, Q to Y) may be employed. The cartridges or materials used in the purification and absorption train should be checked frequently to ensure that their absorbing capacity has not been exhausted.

Reagents

Calcium oxide-lead oxide flux mixture, 50% each by weight. Transfer 25 g each of powdered calcium oxide and lead oxide (Pb_3O_4) to a large silica dish, mix thoroughly, and ignite the mixture in a muffle furnace at approximately 800°C for about 1 hour. Cool, break up any lumps with a small pestle, and store the mixture in a drying oven maintained at approximately 120°C. When in use, store the mixture in a tightly-sealed bottle in a dessicator.

Procedure

In this procedure a blank determination should be carried out either after, or preferably before the analysis of the sample (Notes 2 and 3).

Heat the furnace to 1300 ± 50°C, close the inlet end of the combustion tube with the rubber stopper K (Figure 1), and pass oxygen through the tube at a rate of approximately 1 litre per minute for about 15 minutes to remove air and moisture from the apparatus. Maintain the flow of oxygen, disconnect the carbon dioxide-absorption cartridge c from the purification and absorption unit N, and seal both the outlet and inlet tubes with a single connecting piece of soft rubber tubing. Allow the cartridge to stand in the balance case for 5 minutes, then remove the rubber tubing and quickly weigh the cartridge.

Replace the weighed cartridge in the purification and absorption unit, continue the passage of oxygen, and remove and re-weigh the cartridge at 10-minute intervals until a reasonably constant weight is obtained (Note 4). Replace the cartridge again, open the inlet end of the combustion tube, and quickly insert a previously-ignited covered boat (Note 5), containing 1 g of powdered sample covered with 1 g of the 50% calcium oxide-50% lead oxide flux mixture (Notes 6-8), into the tube. Push the boat into the hot central zone with a steel rod, and immediately close the tube. Continue to pass oxygen through the tube at a rate of approximately 1 litre per minute for 5 minutes, maintain the flow of oxygen, then remove the carbon dioxide-absorption cartridge c and re-weigh (Note 9). Correct the result obtained for the sample by subtracting that obtained for the blank.

Notes

1. The cover employed is usually a sleeve-type, open at both ends to allow free access of oxygen; it prevents damage to the combustion tube if the sample spatters during the combustion process.

2. If the boats and covers have been previously ignited in oxygen at a temperature close to that employed for the combustion of the sample, the magnitude of the blank will depend primarily on the purity of the calcium and lead oxides employed for the flux mixture. It should not exceed approximately 0.5 mg, and successive blanks should agree to within 0.1-0.2 mg.

3. In careful work, the apparatus should be tested for gas-tightness and other possible malfunctions, prior to the analysis of the sample, by analyzing a suitable standard sample of known carbon content.

4. After the apparatus has been swept free of air and the weight of the cartridge is reasonably constant, the blank determination, and the determination of carbon in the standard sample (Note 3) and other samples can be carried out, in succession, as described in the subsequent procedure, if the flow of oxygen is maintained throughout the course of the analyses.

5. To avoid possible contamination from the hands, the pre-ignited boat and cover should be handled with clean tongs or forceps.

6. Because calcium oxide is hygroscopic, previously-weighed samples that are covered with the flux mixture should be stored in a dessicator until required. This also prevents possible contamination of the sample from atmospheric dust.

7. If the sample does not contain fluoride, and contains only small amounts of chloride and/or sulphur compounds, the addition of the calcium and lead oxide flux mixture is not necessary.

8. The calcium and lead oxide flux mixture, and the cartridge (in the purification and absorption unit N) containing manganese dioxide cannot adequately retain and remove, respectively, the oxides of sulphur formed during the combustion of samples containing relatively large amounts of sulphide minerals (e.g., ores and mill products). Samples of high sulphur content can be analyzed by the direct-combustion method if the purification and absorption unit N is replaced by a purification train similar to that shown in the Gravimetric-Evolution Method for carbon dioxide or "carbonate" carbon (p 162, Figure 1, L to Y). If the above train is employed, a suitable trap should be placed between the exit end of the combustion tube and the absorption bulb L containing hydrogen peroxide to prevent possible "suck-back" of liquid into the combustion tube.

Alternatively, oxides of sulphur (and halogen compounds) can be removed by passing the gas formed during the combustion process through granular lead chromate, packed into the exit end of the combustion tube and heated to 300-400°C; sulphur trioxide can be removed by bubbling the gas through a mixture of chromic and phosphoric acids; and sulphur dioxide and sulphur trioxide can be removed by passing the gas through silica gel impregnated with chromic acid[3].

9. If the elemental (graphite) and organic carbon content of the sample is required, this can be calculated from the difference between the total carbon content, determined by the combustion method, and the inorganic "carbonate" carbon content, determined by the Gravimetric-Evolution Method (p 161). However, this indirect method does not yield satisfactory results when the sample contains a large amount of "carbonate" carbon and only a small amount of elemental and organic carbonaceous material. Elemental and organic carbon can be determined directly by the combustion method as follows[3]:

Treat 1 g or more of the sample with concentrated hydrochloric acid to remove carbonate (also some sulphides), filter the solution, using a previously-ignited asbestos pad, and transfer the residue quantitatively to the pad. Dry the pad and residue at 105-110°C, transfer to a combustion boat (omit the addition of the flux mixture), cover the boat, and proceed with the combustion and subsequent determination of carbon.

Slightly low results may be obtained by the above method if the carbonaceous material contains volatile or acid-soluble constituents.

Calculations

$$\% \text{ Total C} = \frac{0.2729 \times (I_S - I_B)}{\text{Sample weight (g)}} \times 100$$

where:

I_S = increase in weight (g) of the carbon dioxide-absorption cartridge for the sample.

I_B = increase in weight (g) of the carbon dioxide-absorption cartridge for the blank.

Other applications

This method can be employed to determine carbon in iron, steel, and ferrous and non-ferrous alloys if a suitable "accelerator" metal or compound is employed as a flux during combustion[1,6].

References

1. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 288-292 (1962).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 770-775 (1953).

3. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 229-230, 431, 436-438 (1968).

4. Idem, ibid., 220 (1968).

5. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E50-68, pp 288-290 (1971).

6. Idem, ibid., pp 11-13, 77-78, 220 (1971).

DETERMINATION OF COPPER IN ORES AND MILL PRODUCTS BY THE ELECTRODEPOSITION METHOD

Principle

Copper is determined by weighing as the metal after electrodeposition on a tared platinum gauze cathode from a dilute sulphuric-nitric acid medium[1].

Outline

The sample is decomposed with hydrochloric, nitric, and hydrofluoric acids. Arsenic, antimony, mercury, tin, and selenium are removed by volatilization as the bromides from a sulphuric acid medium, and the solution is evaporated to dryness. Lead sulphate and acid-insoluble material are ultimately separated by filtration from a nitric acid medium. Silver and residual lead and mercury are subsequently separated from the filtrate as the insoluble chlorides. The acid-insoluble material containing lead sulphate is fused with potassium pyrosulphate, and the melt is dissolved in water. The lead and silver in the resultant solution are separated from the residual copper as the chlorides as described above, and the filtrate is combined with the main solution.

If platinum, palladium, gold, and tellurium are present, copper, the above elements, and certain other elements of the copper and arsenic groups (molybdenum, cadmium, bismuth, and residual lead, tin, arsenic, and antimony) are precipitated as sulphides and separated from iron and various other elements (cobalt, nickel, chromium, aluminum, manganese, zinc, and tungsten) by filtration. After dissolution of the precipitate and re-precipitation of the copper and arsenic group elements to remove occluded elements, the mixed sulphide precipitate is digested in sodium sulphide-sodium hydroxide solution, and the insoluble sulphides of copper, cadmium, bismuth, palladium, and lead are separated from molybdenum, tin, gold, arsenic, antimony, tellurium, and residual tungsten, and from some platinum by filtration. The resultant precipitate is digested in dilute nitric acid, and the solution is filtered to remove palladium sulphide and any tin, platinum, or gold sulphides that were retained in the precipitate. Bismuth, if present, is separated from the copper in the filtrate by a double precipitation as the hydrous oxide with ammonium hydroxide, and the combined filtrate is evaporated to dryness. Copper is ultimately electroplated on a platinum gauze cathode from a dilute sulphuric-nitric acid medium, and the cathode is dried and weighed.

If platinum, palladium, gold, and large amounts of tellurium are absent, the copper in the combined solution obtained after the separation of silver and lead is ultimately precipitated as cuprous thiocyanate from a dilute hydrochloric-tartaric acid medium, and separated from bismuth, iron, and residual arsenic, antimony, and tin by filtration. The precipitate is ignited and the residue is dissolved in dilute nitric acid. Copper is ultimately electroplated from the resulting solution.

Discussion of interferences

Arsenic, antimony, tin, molybdenum, bismuth, mercury, silver, gold, the platinum metals, and selenium and tellurium in the tetravalent states interfere in the determination of copper because they are co-deposited, to some extent, on a platinum cathode. Large amounts of iron interfere by preventing the complete deposition of copper[2,3].

Interference from arsenic, antimony, tin, mercury, and selenium is avoided by volatilizing these elements as the bromides from a hydrobromic-sulphuric acid medium[4]. Interference from silver is avoided by precipitating it as the chloride[1]. Interference from iron, molybdenum, bismuth, tin, antimony, and arsenic can be eliminated by separating copper from these elements, and from cobalt, nickel, zinc, cadmium, manganese, and tungsten by precipitation as cuprous thiocyanate. Lead, gold, tellurium, and the platinum metals (also silver, mercury, and selenium, if present during precipitation) are not separated by this procedure, and co-precipitate, to some extent, with the cuprous thiocyanate[1,3,5]. Gold and the platinum metals interfere in the cuprous thiocyanate method. Lead does not interfere because it is deposited on the anode as the dioxide during electrolysis. Interference from moderate amounts of tellurium (up to approximately 10 mg) is avoided during electrolysis by oxidizing it to the hexavalent state with potassium permanganate, and by conducting the electrolysis in the presence of manganese (II). Manganese (II) is oxidized to permanganate at the anode; this maintains tellurium in the oxidized state and prevents its deposition during electrolysis[2,6].

Interference from platinum, palladium, gold, molybdenum, and large amounts of iron and tellurium is avoided by separating copper and the above interfering elements from iron by precipitation as the sulphides from a 0.4-0.5 M hydrochloric acid medium; the co-precipitated sulphides of the interfering elements are subsequently separated from copper by digestion of the mixed sulphide precipitate in alkaline sodium sulphide[1,3,5] and 2 M nitric acid media[2]. Cadmium, bismuth, rhodium, and osmium are not separated from copper by this procedure. Interference from bismuth is eliminated by separating it from copper by precipitation as the hydrous oxide from an ammoniacal medium[1,3]. Rhodium and osmium interfere in this method. Cadmium does not interfere[1].

Range

The method is suitable for samples containing more than approximately 0.5% of copper.

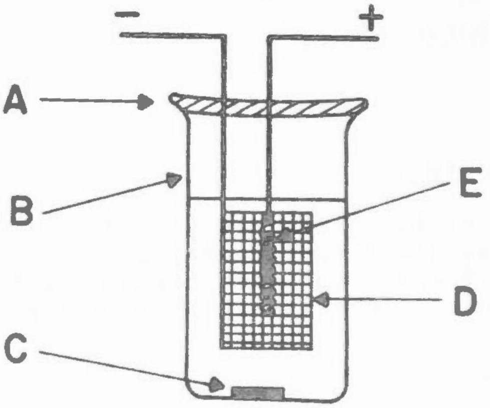

FIGURE 1. Electrolysis unit

A - Split watch glass.
B - Electrolytic beaker (180-ml).
C - Teflon-coated magnet.
D - Platinum gauze cathode (50-mesh, diameter 30 mm, height 50 mm).
E - Platinum spiral-type anode (thickness 1-2 mm, diameter 12 mm, height 50 mm).

Apparatus

Electroplating apparatus with a magnetic stirring mechanism.

Electrolysis unit. Illustrated in Figure 1.

Reagents

Ferric nitrate solution, 15% w/v. Dissolve 15 g of ferric nitrate nonahydrate [$Fe(NO_3)_3.9H_2O$] in water and dilute to 100 ml.

Manganous nitrate solution, 3% w/v. Dissolve 3 g of manganous nitrate hexahydrate in water and dilute to 100 ml.

Bromine water. Water saturated with bromine.

Nitric acid-bromine water solution. Add 50 ml of bromine water to 50 ml of concentrated nitric acid and mix.

Potassium thiocyanate-sodium sulphite solution, 2% and 2% w/v, respectively. Prepare fresh as required.

Potassium permanganate solution, 2% w/v.

Sodium hydroxide solution, 5% w/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% hydrochloric acid saturated with hydrogen sulphide.

Sodium sulphide-sodium hydroxide wash solution. Dissolve 30 g of sodium hydroxide in 1 litre of water and saturate the solution with hydrogen sulphide. Add 3 g of sodium hydroxide, stir to dissolve, and store the solution in a wash-bottle.

Nitric acid wash solution, 13% v/v.

Ammonium hydroxide wash solution, 1% v/v.

Potassium thiocyanate-sodium sulphite wash solution, 0.2% and 0.2% w/v, respectively. Prepare fresh as required.

Sulphuric acid, 50% v/v.

Ammonium sulphamate tablets (1 g).

Procedures

A - Hydrogen sulphide separation procedure in the presence of platinum, palladium, gold, and tellurium

(a) Bismuth absent

Transfer 0.25-1 g of powdered sample, containing approximately 5-200 mg of copper (Note 1), to a 250-ml Teflon beaker, and add 10 ml each of water and concentrated hydrochloric, nitric, and hydrofluoric acids. Cover with a Teflon cover, and boil until the decomposition of acid-soluble material is complete (Note 2). Cool, add 10 ml of concentrated hydrobromic acid and 20 ml of 50% sulphuric acid, boil for several minutes, remove the cover, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, add 10 ml each of concentrated hydrochloric and hydrobromic acids, evaporate the solution to fumes of sulphur trioxide, then repeat the washing and evaporation steps to ensure the complete removal of hydrofluoric, hydrochloric, and hydrobromic acids. Cool, add approximately 25 ml of water, and heat gently to dissolve the soluble salts. Transfer the solution and any residue present, to a 250-ml pyrex beaker and, without baking, evaporate the solution to dryness. Add 20 ml of water and 2 ml of concentrated nitric acid, heat gently to dissolve the salts, and filter the resulting solution (Whatman No. 30 paper) into a 400-ml beaker. Transfer the residue quantitatively to the filter paper, and wash the paper and residue thoroughly with hot water (Note 3). Add 5 ml of 50% sulphuric acid to the filtrate, evaporate it to fumes of sulphur trioxide, cool, wash down the sides of the beaker with water and, without baking, evaporate the solution to dryness. Add 20 ml of water and 2 ml of concentrated hydrochloric acid, and heat gently to dissolve the soluble salts. Filter the solution (Whatman No. 30 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the paper and precipitate.

Transfer the filter paper containing the initial residue to a 30-ml porcelain crucible (Note 4), burn off the paper, and ignite at a low temperature. Fuse the residue with 2-3 g of potassium pyrosulphate, cool, and transfer the crucible and contents to the original 250-ml pyrex beaker. Add approximately 75 ml of water, heat gently until the disintegration of the melt is complete, then remove the crucible after washing it thoroughly with hot water. Add 2 ml of concentrated nitric acid and 5 ml of 50% sulphuric acid to the resulting solution, and evaporate it to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to dryness. Add 20 ml of water and 2 ml of concentrated hydrochloric acid, heat gently to dissolve the soluble salts, and filter the solution (Whatman No. 30 paper) into the beaker containing the main solution. Wash the beaker, paper, and precipitate thoroughly with hot water, and discard the paper and precipitate.

Evaporate the combined solution to approximately 100 ml, add 3 ml of concentrated hydrochloric acid, heat to the boiling point, and pass hydrogen sulphide through the solution for 15 minutes to precipitate copper and various other copper and arsenic group elements. Dilute the solution to 150 ml with water, and continue passing hydrogen sulphide through the solution for a further 10 minutes to ensure the complete precipitation of copper. Filter the solution (Whatman No. 42 paper) (Note 5), and wash the beaker, paper, and precipitate thoroughly with cold hydrogen sulphide wash solution (Note 6). Discard the filtrate and washings.

Using a jet of hot water, transfer the bulk of the precipitate to the beaker in which the precipitation was carried out. Dissolve the small amount of precipitate remaining on the filter paper, using 20 ml of nitric acid-bromine water solution, and wash the paper thoroughly with hot water. Collect the solution in the beaker containing the precipitate, and discard the paper. Add 5 ml of 50% sulphuric acid to the resulting solution, and evaporate it to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water and without baking, evaporate the solution to dryness. Add 5 ml of concentrated hydrochloric acid and 30 ml of water to the residue, heat gently to dissolve the soluble salts, and dilute the solution to approximately 100 ml with water. Pass hydrogen sulphide through the solution for 30 minutes, filter, and wash the paper and precipitate as described above (Note 7).

Using a jet of hot water, return the bulk of the precipitate to the beaker, and dilute the mixture to 125 ml with water. Add 3 g of sodium hydroxide, stir to dissolve, and digest the mixture on a hot-plate for approximately 15 minutes. Pass hydrogen sulphide through the solution for 15 minutes, add an additional 2 g of sodium hydroxide, and stir to dissolve. Filter the resulting solution through the same filter paper, and wash the beaker, paper, and precipitate thoroughly with sodium sulphide-sodium hydroxide wash solution Discard the filtrate and washings.

Return the bulk of the precipitate to the beaker again, dilute the mixture to approximately 90 ml with water, and add 13 ml of concentrated nitric acid. Warm the mixture to dissolve the copper sulphide, filter the solution through the same filter paper, and wash the beaker, paper and precipitate thoroughly with 13% nitric acid. Discard the paper and precipitate. Add 7 ml of 50% sulphuric acid to the resulting solution, and evaporate it to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to dryness. Add approximately 50 ml of water, 6 ml of 50% sulphuric acid, and 2 ml of concentrated nitric acid, and heat gently to dissolve the residue. Transfer the solution to a 180-ml electrolytic beaker containing a Teflon-coated magnet, cool, and dilute to 100 ml with water.

Connect a clean, tared, platinum gauze cathode, and a clean platinum anode (Note 8) to the electroplating apparatus as shown in Figure 1, and lower the electrodes into the solution so that the cathode is nearly, but not entirely covered by the solution. Cover the beaker with a split watch glass, turn on the stirring mechanism, and electrolyze the solution at a current of 2 amperes and an applied potential of 4-5 volts for approximately 45 minutes or until the blue colour of the copper has entirely disappeared (Note 9). Add an ammonium sulphamate tablet (Note 10), continue the electrolysis for a further 15 minutes, then remove the watch glass, wash down the electrode stems and the sides of the beaker with water, and add sufficient water to cover the cathode. Continue the electrolysis until the deposition of copper is complete, as indicated by failure of copper to plate on the freshly immersed surface of the cathode, or on a new surface of the electrode stem when the level of the solution is raised by the addition of water. Without interrupting the current, gradually raise the electrodes from the solution while directing a stream of water from a wash-bottle against the exposed part of the cathode (Note 11). Disconnect the cathode, dip it into a beaker of water to remove the acid, then into two successive beakers containing ethyl or methyl alcohol to remove the water. Dry the cathode in an oven at 100-110°C for 3 minutes (Notes 12 and 13), cool in a dessicator and weigh (Note 14).

(b) Bismuth present

Following the digestion of the mixed sulphide precipitate, obtained by passage of hydrogen sulphide through the alkaline sodium hydroxide solution, in 13% nitric acid, and evaporation of the resulting solution to fumes of sulphur trioxide, cool, and dilute the solution to approximately 100 ml with water. If necessary (Note 15), add 1-2 ml of 15% ferric nitrate solution, and heat the solution to the boiling point. Using litmus paper, neutralize the solution approximately with concentrated ammonium hydroxide, and add 10-15 ml in excess. Boil the resulting solution for several minutes to coagulate the precipitate, allow the precipitate to settle, and filter the solution (Whatman No. 541 paper) into a 600-ml beaker. Wash the beaker, paper, and precipitate thoroughly with warm 1% ammonium hydroxide, then, using a jet of hot water, transfer the bulk of the precipitate to the beaker in which the precipitation was carried out. Dissolve the small amount of precipitate remaining on the filter paper, using hot 13% nitric acid, and wash the paper thoroughly with hot water. Collect the resulting solution in the beaker containing the precipitate, and discard the paper. If necessary, add sufficient concentrated nitric acid to dissolve the precipitate, then add 5 ml in excess, and re-precipitate, filter, and wash the precipitate as described above. Collect the filtrate and washings in the beaker containing the initial filtrate, and discard the paper and precipitate.

Evaporate the combined filtrates to approximately 150 ml, add 10 ml of 50% sulphuric acid and 20 ml each of concentrated nitric and hydrochloric acids, cover the beaker, and boil the solution for approximately 30 minutes to destroy the ammonium salts. Remove the cover, evaporate the solution to approximately 50 ml, then repeat the treatment with nitric and hydrochloric acids, using 10 ml of each, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to dryness. Add approximately 50 ml of water, 6 ml of 50% sulphuric acid, and 2 ml of concentrated nitric acid, and heat gently to dissolve the residue. Transfer the resulting solution to a 180-ml electrolytic beaker containing a Teflon-coated magnet, dilute to 100 ml with water, and proceed with the electrolysis of copper as described above.

B - Cuprous thiocyanate separation procedure in the absence of platinum, palladium, gold, and 10 mg or more of tellurium

Following sample decomposition and the separation of silver and lead from the initial filtrate and the subsequent solution of the acid-insoluble residue by precipitation as the chlorides as described in Procedure A (a), evaporate the combined filtrates to approximately 150 ml (Note 16). Carefully add 5% sodium hydroxide solution until a permanent precipitate begins to form, then add sufficient concentrated hydrochloric acid, by drops, to dissolve the precipitate. Add 1 ml in excess (Note 17), then add 2-3 g of tartaric acid and stir to dissolve. Add 2 g of sodium sulphite, dilute to approximately 200 ml with water (Note 18), and heat the solution almost to the boiling point. By burette, and while stirring, add 2% potassium thiocyanate solution, by drops, until no further precipitation of cuprous thiocyanate is apparent, then add a three-fold excess (Note 19) and allow the solution to stand for 4 hours or preferably overnight. Filter the solution (Whatman No. 42 paper), transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate thoroughly with cool 0.2% potassium thiocyanate-0.2% sodium sulphite solution. Discard the filtrate and washings.

Transfer the paper and precipitate to a 30-ml porcelain crucible, burn off the paper, and ignite at a low temperature. Cool, add 10 ml of water and 2 ml of concentrated nitric acid, warm gently to dissolve the residue, and tranfer the resulting solution to a 180-ml electrolytic beaker containing a Teflon-coated magnet. Add 6 ml of 50% sulphuric acid and dilute the solution to approximately 90 ml with water. Add 2% potassium permanganate solution, by drops, until a faint permanent pink tint is obtained, then add 5 ml of 3% manganous nitrate solution, and proceed with the electrolysis of copper as described above.

Notes

1. More than approximately 200 mg of copper cannot be conveniently handled by this method because of the bulkiness of the mixed sulphide or cuprous thiocyanate precipitate.

2. If the sample contains an appreciable amount of sulphides, additional hydrochloric and nitric acids may be required to obtain complete decomposition.

3. The subsequent ignition and fusion of the acid-insoluble residue may be omitted if only a small amount of light-coloured residue is present.

4. Residues containing sulphates, sulphides, or other salts of easily reducible elements (e.g., lead, silver, mercury, bismuth, antimony, tin, and arsenic) should not be ignited in platinum crucibles. These elements may be reduced to the metallic state by the carbon from the filter paper, or by reducing gases from the flame, and will subsequently alloy with, and contaminate the crucible.

5. Because cuprous sulphide is easily oxidized or rendered colloidal, the filter paper should be kept at least two-thirds full of solution during filtration and washing to avoid undue exposure of the sulphide precipitate to air[5].

6. If the amount of precipitate obtained is small, the re-precipitation of the mixed sulphides, and the subsequent alkaline-hydrogen sulphide separation procedure can be omitted. Instead, wash the precipitate thoroughly with sodium sulphide-sodium hydroxide wash solution, and proceed as described.

7. If the sample is known to contain only small amounts of arsenic, antimony, tin, molybdenum, selenium, and/or tellurium, omit the subsequent alkaline-hydrogen sulphide separation procedure, wash the precipitate thoroughly with sodium sulphide-sodium hydroxide wash solution, and proceed as described.

8. Previously deposited metals can usually be removed from platinum gauze cathodes by treatment with concentrated or hot 30% nitric acid. After washing thoroughly with water, the cathode should be dried at 110-120°C, cooled, and weighed before electrolysis. Lead dioxide can be removed from platinum anodes by treatment with dilute nitric acid containing hydrogen peroxide.

9. Slow deposition, without stirring, yields a more accurate result for copper[1-3]. If this method is employed, electrolyze the solution for approximately 16 hours, or preferably overnight at a current of 0.5-0.6 amperes and an applied potential of approximately 2 volts. Add an ammonium sulphamate tablet when the colour of the copper has disappeared, and proceed as described until the deposition of copper is complete.

10. Unless the nitric acid added to the sample solution, prior to electrolysis, was freshly boiled to remove nitrous acid, ammonium sulphamate should be added to destroy any nitrous acid that may be present in the electrolyte. Nitrous acid prevents complete deposition of copper, and also dissolves copper that has been deposited[3].

11. Because partial dissolution of the copper deposit will occur in the presence of acid, the current should not be shut off as long as the electrodes are in the acidic solution, and the cathode should be washed thoroughly with water to remove the acid.

12. The drying of the cathode at 100-110 °C should not be prolonged because some copper may be converted to the oxide.

13. The copper deposit should be adherent, silky in texture, and a salmon-pink colour. Dullness in colour indicates oxidation or the presence of foreign elements. If it is dark-coloured or appears spongy or crystalline, dissolve the deposit in 100 ml of 2% nitric acid, add 6 ml of 50% sulphuric acid and re-electrolyze the solution.

14. In exact work, the electrolyte remaining after the deposition of copper should be evaporated to dryness and subsequently analyzed for residual copper either by atomic-

absorption spectrophotometry (p 15) or spectrophotometrically by the Cuproine Method (p 53). The amount (g) of copper obtained should be added to the weight of the electrolytic deposit.

15. If the amount of bismuth present is very small, it is advantageous to add a small amount of iron (III) as a collector, and subsequently precipitate the hydrous oxide of bismuth by occlusion with hydrous ferric oxide[3]. One ml of 15% ferric nitrate nonahydrate solution contains approximately 21 mg of iron (III).

16. If the sample contains an appreciable amount of tungsten, any insoluble tungsten compounds that may have precipitated during evaporation of the solution will re-dissolve completely when the solution is subsequently heated.

17. More than 1 ml of concentrated hydrochloric acid should not be added because the precipitation of copper as cuprous thiocyanate is quantitative only in weakly acid solutions. The precipitate is appreciably soluble in solutions containing excess acid[7].

18. If the solution does not emit a strong odor of sulphur dioxide at this point, add more sodium sulphite to ensure the complete reduction of the copper.

19. An excess of potassium thiocyanate is required for the quantitative precipitation of cuprous thiocyanate, but too large an excess is undesirable because the precipitate is partly soluble in strong thiocyanate solutions. The concentration of excess potassium thiocyanate should not exceed 0.05 M (i.e., approximately 1 g in 200 ml of solution)[7]. According to the reaction

$$2\ Cu^+ + 2\ KSCN \rightarrow 2CuSCN + 2K^+,$$

200 mg of copper react with 306 mg of potassium thiocyanate (i.e., 15.3 ml of a 2% solution).

Calculations

$$\%Cu = \frac{\text{Weight of dried deposit (g)}}{\text{Sample weight (g)}} \times 100$$

References

1. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Mines Branch Monograph 866, Method No. Cu-1, Part III, April (1958).
2. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 3, pp 9-10, 15-16, 24-26 (1961).
3. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 398-404 (1962).
4. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, pp 72-74 (1959).
5. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 243-253 (1953).
6. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E 121-60, 607 (1971).
7. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, 701 (1948).

DETERMINATION OF MAGNESIUM IN ACID-SOLUBLE AND REFRACTORY SILICATE ROCKS AND MINERALS, CARBONATE ROCKS, CLAY, SHALE, AND IRON, CHROMIUM, TITANIUM, MOLYBDENUM AND SULPHIDE ORES AND MILL PRODUCTS BY PRECIPITATION WITH DIBASIC AMMONIUM PHOSPHATE

Principle

This method[1,2] is based on the precipitation of magnesium as magnesium ammonium phosphate from a strongly ammoniacal medium. Magnesium is determined by weighing as the pyrophosphate after ignition of the precipitate.

The corresponding reactions for these processes are:

$$MgCl_2 + (NH_4)_2HPO_4 + NH_4OH + 6H_2O \rightarrow MgNH_4PO_4\cdot 6H_2O + 2NH_4Cl + H_2O$$

$$2MgNH_4PO_4.6H_2O \xrightarrow{\text{ignition}} Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Outline

Following the separation of calcium by double precipitation as the oxalate as described in the Volumetric-Oxalate Method for calcium (p 243, Note 20), the combined filtrates and washings are acidified with sulphuric acid. After decomposition of the excess ammonium salts, the solution is evaporated to dryness to remove sulphuric acid. Barium sulphate, if present, and extraneous silica are ultimately removed by filtration. Magnesium is precipitated as magnesium ammonium phosphate from a strongly ammoniacal medium, and separated from sodium, potassium, and various other elements (chromium VI and vanadium V) by filtration. After dissolution of the precipitate and re-precipitation of the magnesium to remove occluded elements, the resulting precipitate is ignited and weighed.

Discussion of interferences

With the possible exception of barium, chromium (VI), and vanadium (V), depending on the history of the sample solution, the majority of the elements that interfere in the precipitation and/or determination of magnesium by forming insoluble hydrous oxides or phosphates will have been previously separated from magnesium by one or more of the separation procedures (i.e., mercury cathode electrolysis, cupferron-chloroform extraction, and hydrogen sulphide and ammonium hydroxide precipitations) described in the Volumetric-Oxalate Method for Calcium (p 241) and in the Gravimetric-Ammonium Hydroxide (p 141) and 8-Hydroxyquinoline (p 151) Methods for aluminum.

Interference from carbonate and phosphate, which cause low results for magnesium because of the formation of insoluble magnesium compounds, is avoided during the preliminary ammonium hydroxide separation of aluminum and other hydrous oxides by employing carbonate-free ammonium hydroxide for precipitation, and by co-precipitating phosphate, when necessary, as ferric phosphate in the presence of excess iron (III)[3]. Manganese, which interferes by forming an insoluble phosphate that co-precipitates with magnesium ammonium phosphate[1,2], is separated from magnesium, prior to the separation of calcium as the oxalate, by oxidizing it to the dioxide with ammonium persulphate in a weakly acid medium; the dioxide is subsequently occluded with the hydrous oxide of zirconium in a weakly ammoniacal medium[4]. Barium, which also co-precipitates partially as an insoluble phosphate, is separated from magnesium as the insoluble sulphate. Chromium (VI) and vanadium (V) do not interfere[2,5].

Excess amounts of ammonium salts, particularly ammonium oxalate, that remain in the filtrate after the separation of calcium, retard the precipitation of small amounts of magnesium[1,2]. Possible negative error from large amounts of ammonium chloride and ammonium oxalate is avoided by destroying these compounds by evaporation of the filtrate with nitric, hydrochloric and sulphuric acids[1].

Excess amounts of sodium and, particularly potassium salts cause the initial magnesium precipitate to be impure because of the substitution of the alkali metal ion for the ammonium radical. The initial precipitate may also be contaminated by other magnesium phosphates [i.e., $Mg_3(PO_4)_2$and/or $Mg(NH_4)_4(PO_4)_2$] which cause error in the magnesium result because they are not converted to magnesium pyrophosphate during the ignition of the precipitate[2]. Error from alkali salts, and contamination from other magnesium phosphate compounds is eliminated by dissolving the initial precipitate and re-precipitating the magnesium, under controlled conditions, in the presence of a minimum amount of ammonium salts and only a slight excess of dibasic ammonium phosphate[1,2].

Small amounts of calcium, that remain in the filtrate after the separation of calcium as the oxalate, co-precipitate with magnesium as calcium phosphate and cause high results for magnesium[1,2,5]. The result obtained can be corrected for positive error from calcium by dissolving the ignited residue in a suitable acid, determining its calcium phosphate content by atomic-absorption spectrophotometry, and subtracting the amount obtained from the weight of the ignited residue.

Range

The method is suitable for samples containing more than approximately 0.1% of magnesium.

Reagents

Dibasic ammonium phosphate solution, 10% w/v. Prepare fresh as required and filter the solution before use.

Sulphuric acid, 50% v/v.

Hydrochloric acid, 5% v/v.

Ammonium hydroxide wash solution, 5% v/v.

Procedure

Following the separation of calcium by precipitation as the oxalate as described in the Volumetric-Oxalate Method for calcium (p 243, Note 20) (Notes 1 and 2), add 30 ml of 50% sulphuric acid to the combined filtrates and washings obtained after the double oxalate separation, and evaporate the solution to approximately 150 ml. Add 60 ml of concentrated nitric acid and 30 ml of concentrated hydrochloric acid, cover the beaker, heat gently until the vigorous reaction ceases, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, add approximately 20 ml of water, repeat the nitric and hydrochloric acid treatment, and carefully evaporate the solution to dryness. Add 2-3 ml of concentrated hydrochloric acid and approximately 100 ml of water to the residue, and heat gently until the solution is clear. Filter the solution (Whatman No. 42 paper) into a 600 ml beaker to remove barium sulphate and extraneous silica, and wash the beaker, paper, and precipitate thoroughly with water (Note 3). Discard the paper and precipitate.

Dilute the resulting solution to 250 ml with water, add sufficient filtered 10% dibasic ammonium phosphate solution so that approximately 1 g of the reagent is present for each 100 ml of solution, and add 10 ml in excess. Add a small piece of red litmus paper and, while stirring vigorously (Note 4), slowly add concentrated ammonium hydroxide until the solution is alkaline. Add 10 ml in excess for each 100 ml of solution, continue stirring until the precipitate starts to form (Note 5), then cover the beaker and allow the solution to stand overnight. Filter the solution (Whatman No. 42 paper), retain as much of the precipitate as possible in the beaker, and wash the precipitate in the beaker 3 or 4 times, by decantation, with cold 5% ammonium hydroxide. Filter the washings through the paper, then wash the paper and precipitate 4 times with 5% ammonium hydroxide. Discard the filtrate.

Wash down the sides of the beaker containing the precipitate with a small amount of hot 5% hydrochloric acid, add a small further portion, if necessary, to dissolve the precipitate, and heat the solution to the boiling point. Place a 250-ml beaker under the funnel, and pour the hot solution through the filter paper. Wash the beaker thoroughly with small portions of hot 5% hydrochloric acid, and pour the washings through the paper. Wash the paper thoroughly, including the inside flap, with small portions of the hot acid solution, then remove and discard the paper, and wash the funnel once or twice with the acid solution.

Dilute the resulting solution to approximately 100 ml with water, add 1 ml of 10% dibasic ammonium phosphate solution, and cool the solution to about 10°C. Slowly, and while stirring (Note 4), add concentrated ammonium hydroxide, by drops, until a precipitate forms, and allow the precipitate to settle. Continue adding 1-ml portions of the phosphate solution, and allow the precipitate to settle each time, until the precipitation of magnesium is complete (Note 6), then add 10 ml of concentrated ammonium hydroxide, and allow the solution to stand for at least 4 hours or preferably overnight. Filter the solution (Whatman No. 42 paper), transfer the precipitate quantitatively to the filter paper, and wash the beaker 3 or 4 times with cold 5% ammonium hydroxide. Wash the paper and precipitate 10 times with 5% ammonium hydroxide, then once with water, and discard the filtrate.

Transfer the paper and precipitate (Note 7) to a tared 30-ml platinum crucible, partly cover the crucible with a platinum cover and, starting with a cold muffle furnace, dry and burn off the paper at as low a temperature as possible (Note 8). Ignite the precipitate at approximately 1100°C (Note 9) for 30 minutes, cool in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained (Note 10).

Notes

1. Low concentrations of magnesium (particularly 1% or less) in acid-soluble silicate rocks and minerals, clay, shale (also limestone), and iron ores and concentrates should preferably be determined by the appropriate atomic-absorption spectrophotometric methods described for these sample materials (pp 3 and 7). Small amounts in chromium, titanium, molybdenum and sulphide ores and mill products, and in iron ores and mill products can be determined by atomic-absorption spectrophotometry, after sample decomposition (using a fresh portion of the sample) and separation of the matrix elements by the mercury cathode and cupferron-chloroform separation procedures described in the Gravimetric-8-Hydroxyquinoline Method for aluminum (p 151). The resulting solution should subsequently be evaporated to dryness to remove excess sulphuric or perchloric acids, followed by dissolution of the residue in water or a suitable dilute acid. In all of the above methods the resulting solutions can also be used for the determination of calcium by atomic-absorption spectrophotometry.

2. If the sample or aliquot of the sample solution contains an appreciable amount of magnesium (e.g., dolomite), and extreme accuracy is not required, the subsequent removal of the excess ammonium chloride and ammonium oxalate by treatment of the solution with nitric, hydrochloric, and sulphuric acids can be omitted. In this case, neutralize the combined solution approximately with concentrated hydrochloric acid, and add 3 or 4 ml in excess. If barium is present, add sufficient 50% sulphuric acid, by drops, to precipitate the barium as the sulphate, filter the solution, then proceed with the initial precipitation of magnesium ammonium phosphate. However, if this procedure is employed, care must be taken that the requisite increments of dibasic ammonium phosphate solution and concentrated ammonium hydroxide are added to compensate for the larger volume of the sample solution.

If the sample or aliquot contains only small amounts of magnesium (e.g., limestone), the excess ammonium chloride and ammonium oxalate should be destroyed prior to the precipitation of magnesium[1,2].

3. If desired, up to approximately 30 mg of magnesium can be precipitated at this stage as the 8-hydroxyquinolate compound, in the absence of excess ammonium salts, and determined either gravimetrically or volumetrically (by bromometric titration) according to the procedures described by Maxwell (pp 374-375)[1] or Hillebrand et al (pp 642-644)[2]. However, vanadium may interfere if it was not removed prior to the precipitation of calcium as the oxalate[6].

4. If a glass stirring rod is used and an appreciable amount of magnesium is present, the sides of the beaker should not be scraped with the rod during stirring of the solution. The abrasion of the glass surface encourages the growth of tiny crystals of the precipitate which adhere to the walls of the beaker and which are difficult to transfer quantitatively to the filter paper[1,2].

5. If only a small amount of magnesium is present, precipitation can sometimes be initiated by scraping the sides of the beaker with a glass rod (Note 4)[1], and can be hastened by cooling the solution to 0-10°C and stirring vigorously[2].

6. Complete precipitation of magnesium is indicated when no further formation of a precipitate occurs on the addition of a drop of concentrated ammonium hydroxide to the supernatant solution[1].

7. To ensure the recovery of any of the magnesium precipitate that may have adhered to the beaker, funnel, and stirring rod during the filtration step, wipe the rod and the top inner parts of the beaker and funnel with small moistened pieces of filter paper, and add the paper to the platinum crucible containing the precipitate.

8. Because carbon from the filter paper may become entrapped in the resultant magnesium pyrophosphate and virtually "fireproofed", the charring of the paper and oxidation of the carbon must be carried out slowly at 450°C or less. The crucible should never be allowed to become more than a very faint red before all of the carbon has disappeared[1].

9. If the magnesium precipitate is ignited at temperatures appreciably higher than 1100°C, phosphorus may be lost, presumably by volatilization, or phosphate may be reduced and cause damage to the platinum crucible. At appreciably lower temperatures, the conversion of magnesium ammonium phosphate to pyrophosphate is slow[1]. The final residue is usually a slightly gray colour.

10. A small amount of calcium, resulting from the slight solubility of calcium oxalate in aqueous media, usually remains in the combined filtrate and washings obtained after the separation of calcium as the oxalate. This residual calcium is co-precipitated as the phosphate during the precipitation of magnesium ammonium phosphate and contaminates the precipitate[1,2,5]. In exact work, a correction for co-precipitated calcium phosphate can be made by dissolving the ignited magnesium pyrophosphate residue in hydrochloric or nitric acid, diluting the solution to a definite volume with water, and determining the amount of calcium present by atomic-absorption spectrophotometry. The amount obtained can then be calculated as calcium phosphate and subtracted from the weight of the residue.

$Ca_3(PO_4)_2$ (g) = 7.740 x Ca (g).

The ignited residue may also be contaminated with manganese pyrophosphate, as indicated by a brown or pinkish colour, if the manganese separation was not carried out as described prior to the separation of calcium as the oxalate[1,2,5]. After dissolution of the residue as described above, a correction for manganese can also be made, in a similar manner to that for calcium, by determining the amount of manganese present, either by atomic-absorption spectrophotometry or by the Spectrophotometric-Permanganate Method (p 57), followed by calculation to manganese pyrophosphate, and subtraction of the amount obtained from the weight of the ignited residue[1,2].

$Mn_2P_2O_7$ (g) = 2.583 x Mn (g).

Calculations

$$\%MgO = \frac{0.3623 \times \text{Weight of ignited precipitate(g)}}{S} \times 100$$

where:

S = weight (g) of the sample in the solution or aliquot taken for analysis.

%Mg = 0.6032 x % MgO

$\%MgCO_3$ = 2.092 x % MgO

Other applications

This method can be employed to determine magnesium in fire-brick, glass, cement, and bauxite.

References

1. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 163-166, 372-374 (1968).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 632-642 (1953).

3. Idem, ibid., pp 621-622 (1953).

4. L.C. Peck, "Systematic Analysis of Silicates", U.S. Geol. Surv. Bull., 1170, pp 30-31, 66 (1964).

5. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 68-71 (1938).

6. Idem, ibid., pp 113-116 (1938).

DETERMINATION OF MOISTURE, AND TOTAL AND COMBINED WATER IN ORES AND MILL PRODUCTS, SILICATE ROCKS AND MINERALS, SILICA SAND, SANDSTONE, QUARTZITE, CARBONATE ROCKS, CLAY, AND SHALE

Principle

Hygroscopic moisture, designated as H_2O^-, $H_2O<110°C$, or non-essential water, is determined from the loss in weight of the sample after heating at 105-110°C[1-4]. The method for the determination of total water[1-3,5-7] is based on the liberation of water by ignition of the sample in a water-free oxygen atmosphere, and the collection of the resultant water vapour in a weighed absorption bulb containing anhydrous magnesium perchlorate. Total water is determined from the increase in weight of the absorption bulb. Combined water, designated as H_2O^+, $H_2O>110°C$, water of constitution, essential, or bound water, is determined from the difference between the total water content and the moisture content of the sample.

Outline

To determine moisture, the weighed sample is heated for 1 hour at 105-110°C, cooled and re-weighed.

To determine total water, the sample is covered with a mixture of calcium and lead oxides, and ignited at a high temperature in a combustion tube in a water-free oxygen atmosphere. The resultant water vapour is collected in a weighed absorption bulb, and the bulb is re-weighed.

Discussion of interferences

Combined water (H_2O^+) and hygroscopic moisture (H_2O^-) are relatively arbitrary divisions of the total water content of the sample because of the numerous factors that can affect the accurate determination of both fractions. Hygroscopic moisture depends on the degree of comminution of the sample, on whether it contains hygroscopic constituents, and on the relative humidity of the atmosphere at the time the sample is weighed. Grinding of the sample can cause either a positive change in the moisture content because of the consequent greater surface area that is available for the adsorption of water,or a negative change because of the heat and pressure that are developed during the grinding process[1-4]. Excessive grinding can cause low results for combined water if the resultant heat is sufficient to cause partial volatilization of water of crystallization[2]. High results will be obtained for hygroscopic moisture and, subsequently low results for combined water if the sample contains "loosely-bound" water (e.g., some zeolites), or water of crystallization that is partly or completely expelled when the sample is heated to 105-110°C[1-3]. Low results will be obtained for hygroscopic moisture if the sample contains ferrous compounds that are readily oxidized to heavier ferric compounds during the heating stage. High results will be obtained for extremely hygroscopic samples (e.g., rocks containing chlorite) because of the difficulty in weighing these samples accurately, particularly after drying at 105-110°C[7]. Possible error, which can occur in the determination of combined water because of hourly or daily fluctuations in relative atmospheric humidity, should be minimized by determining the hygroscopic moisture and total water contents of the sample either concurrently, or at least on the same day.

Chlorine, fluorine, oxides of sulphur, and volatile acid compounds that may be produced during the ignition of samples containing chloride, fluoride, sulphate, or sulphide compounds interfere in the determination of total water because they are partly absorbed by the anhydrous magnesium perchlorate employed for the absorption of the liberated water vapour[1-7].

Moderate amounts of the above gases and acidic compounds are prevented from volatilizing during ignition by covering the sample with a retentive flux mixture of calcium and lead oxides[4]. The flux mixture also prevents the reduction of water to hydrogen by ferrous iron in the sample[4,8]. Large amounts of

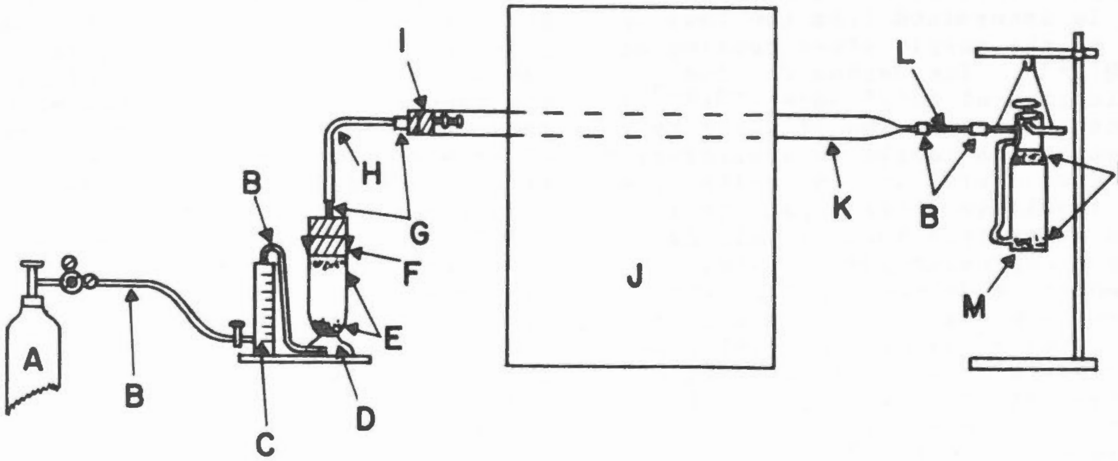

FIGURE 1. Apparatus for the determination of total water

A - Oxygen tank with two-stage regulator.
B - Rubber tubing.
C - Oxygen-flow meter.
D - Drying unit containing anhydrous magnesium perchlorate (Anhydrone).
E - Glass-wool.
F - Rubber stopper.
G - Glass tube.
H - Tygon tubing (approximately 2.5 ft.).
I - Rubber stopper with oxygen (heat-deflector) baffle.
J - Electric furnace, resistance-type with appropriate temperature controls, or induction-type with appropriate power input indicating device.
K - Combustion tube.
L - Glass tube (approximately 2 in. in length) packed with glass-wool.
M - Absorption bulb (Nesbitt-type) containing anyhdrous magnesium perchlorate.

sulphur oxides and acidic sulphur compounds can be removed from the liberated water vapour, as lead sulphate, by passing the water vapour through a heated column packed with a mixture of lead oxides[3] or with granular lead chromate[7].

Carbon dioxide does not interfere in this method[1-7]. Organic material causes high results for total water because it is oxidized to water and carbon dioxide during the ignition of the sample[1,2,4-6,8].

A purification unit containing anhydrous magnesium perchlorate removes water from the oxygen employed as the carrier gas.

Range

The methods for hygroscopic moisture and total water are suitable for samples containing more than approximately 0.1% of moisture or water.

Apparatus

Apparatus for the determination of total water. A typical arrangement of the apparatus is illustrated in Figure 1. The following general recommendations indicate the type of apparatus and related materials that are acceptable:

(a) *Electric furnace* - Any furnace that will heat the sample to the required temperature, including split-type furnaces with wire-wound heating elements, may be employed.

(b) *Combustion tubes* - Translucent silica or Vitreosil tubes that are gas-tight at operating temperatures may be used. Tubes approximately 30 inches long, with an inside diameter of 1.25 inches, and tapered at one end are generally used with resistance furnaces.

(c) *Boats and covers* - Alundum, Vitreosil, clay, or zircon boats and covers may be employed (Note 1). Prior to use, the boats and covers should be pre-ignited in air, at approximately 1000°C, for at least 15 minutes, then stored in a drying oven maintained at approximately 120°C.

(d) *Oxygen-purification unit* - The purity of the oxygen should be not less than 99.5%. It should be passed through two reduction pressure valves (approximately 30 and 2 to 4 psi, respectively) or a suitable two-stage reduction valve to provide a steady and adequate flow. Organic material of any kind is an undesirable impurity. It is usually absent in commercial oxygen, and it generally suffices to remove water by passing the gas through anhydrous magnesium perchlorate. If the presence of organic material is suspected, the oxygen should first be passed through a tube that is loosely-packed with copper oxide and heated to about 450°C.

(e) *Water-absorption unit* - A Nesbitt-type absorption bulb (shown in Figure 1) or a commercial absorption cartridge (e.g., that employed in the Burrell Carbotrane) may be employed. If a Nesbitt bulb is used, the stopcock should be lubricated with silicone stopcock grease. The glass tube L (Figure 1), employed to connect the absorption bulb to the exit end of the combustion tube, should be relatively short so that the hot exit gas which carries the resultant water vapour is not cooled to such an extent that appreciable condensation of the water vapour occurs in the tube. The tube should also be packed with glass-wool to screen out finely-divided solid particles. All connections between the exit end of the combustion tube and the inlet tube of the absorption bulb should be, as nearly as possible, glass-to-glass with the least possible inside exposure of rubber. The magnesium perchlorate used in the absorption bulb should be checked frequently to ensure that its absorbing capacity has not been exhausted.

Reagents

Calcium oxide-lead oxide flux mixture, 50% each by weight. Transfer 25 g each of powdered calcium oxide and lead oxide (Pb_3O_4) to a large silica dish, mix thoroughly, and ignite the mixture in a muffle furnace at approximately 800°C for about 1 hour. Cool, break up any lumps with a small pestle, and store the mixture in a drying oven maintained at approximately 120°C.

When in use, store the mixture in a tightly-sealed bottle in a dessicator.

Procedures

Determination of moisture

Transfer 1 g of powdered sample to a tared, covered 30-ml platinum crucible (Note 2), and re-weigh the crucible, cover, and contents (Note 3). Remove the cover and heat the crucible in a drying oven at 105-110°C for 1 hour. Re-cover the crucible, cool in a dessicator for approximately 30 minutes, then remove the cover for a moment and re-weigh (Notes 4 and 5).

Determination of total water

In this procedure a blank determination should be carried out either after, or preferably before the analysis of the sample (Note 6).

Heat the furnace to 1000 ± 25°C, close the inlet end of the combustion tube with the rubber stopper I (Figure 1), and pass oxygen through the tube at a rate of approximately 1 litre per minute for about 15 minutes to remove air and moisture from the apparatus. Maintain the flow of oxygen, disconnect the water-absorption bulb M (Note 7), quickly close the stopcock in the bulb, and place the bulb in the balance case. When the bulb is cool, open the stopcock for a moment to equalize the pressure and weigh. Open the stopcock and quickly re-connect the bulb to the apparatus. Continue the passage of oxygen, and remove and re-weigh the bulb at 10-minute intervals until a reasonably constant weight is obtained (Note 8).

Re-connect the bulb again, open the inlet end of the combustion tube and, depending on the expected water content, quickly insert a previously-ignited covered boat (Note 9), containing 0.5-1 g of powdered sample covered with 1 g of the 50% calcium oxide-50% lead oxide flux mixture (Notes 10-13), into the tube. Push the boat into the hot central zone with a steel rod, and immediately close the tube. Continue to pass oxygen through the tube at a rate of approximately 1 litre per minute until all of the water has been expelled from the sample (Note 14), then remove the water-absorption bulb and re-weigh. Correct the result obtained for the sample by subtracting that obtained for the blank.

Notes

1. The cover employed is usually a sleeve-type, open at both ends to allow free access of oxygen; it prevents damage to the combustion tube if the sample spatters during the ignition process.

2. Cylindrical low-form weighing bottles, platinum dishes, and Vitreosil, porcelain, or nickel crucibles can also be employed for the determination of moisture. However, if a platinum crucible is used, the subsequent dried sample (i.e., silicate rocks and minerals, clay, shale, silica sand, sandstone, and quartzite) can be used for the determination of silica by the Classical-Gravimetric Method (Procedures C (a) and C (b), p 201).
If a platinum dish is employed the dried sample (i.e., silica sand, sandstone, and quartzite) can be used for the determination of silica by the Gravimetric-Indirect Rapid Control Method (p 207) involving the direct volatilization of silicon as the tetrafluoride.

3. Error due to possible loss of sample during the transfer of the sample to the crucible is eliminated by re-weighing the crucible and contents, and calculating the weight of the contents. If the weights of the sample by direct weighing and by difference do not agree to within 0.2 mg, either the sample is hygroscopic, or the transfer of the sample to the crucible was carelessly made[8].

4. If the loss in weight exceeds 1 mg, the heating, cooling, and weighing should be repeated until constant weight is obtained. If the loss exceeds 5 mg, the crucible should be heated at a slightly higher temperature (e.g., 125°C) to determine whether a further loss in weight, indicating the presence of a significant amount of hydrous material (e.g., water of crystallization), occurs[4].

5. Constant weight (Note 4) may be difficult to obtain if the sample contains organic material. In this case, the loss in weight after a single heating can be arbitrarily considered to represent the moisture in the sample[4].

6. If the boats and covers have been previously ignited at 1000°C and stored in a drying oven, the magnitude of the blank will depend primarily on the dryness of the calcium and lead oxide mixture employed as the flux (Note 11), and on the atmospheric humidity. If humid conditions prevail, several blank determinations should be made. The magnitude of the blank should not exceed approximately 0.5 mg, and successive blanks should agree to within 0.1-0.2 mg.

7. Two weighed water-absorption bulbs can be used in the apparatus, if desired. This will ensure the complete absorption of water vapour, and provides an indication when the first bulb must be re-charged.

8. After the apparatus has been swept free of air and moisture and the weight of the absorption bulb is reasonably constant, the blank determination(s) and the determination of water in the sample or samples can be carried out, in succession, as described in the subsequent procedure, if the flow of oxygen is maintained throughout the course of the analyses.

9. To avoid contamination by moisture from the hands, the boat and cover should be handled with clean tongs or forceps.

10. If only the combined water content of the sample is required, this can be determined directly by analyzing a suitable portion of sample that has been previously dried at 105-110°C.

11. Because calcium oxide is hygroscopic, the flux mixture should be weighed quickly and added to the sample just prior to the introduction of the boat and sample into the combustion tube.

12. The calcium and lead oxide flux mixture, and the temperature employed in this method may not be adequate for the determination of total water in certain minerals (e.g., talc, topaz, tourmaline, staurolite, chondrodite, titanite, epidote, hornblende, and hydroxyapatite) and micas (e.g., phlogopite) that require a temperature of approximately 1200°C for the complete expulsion of their water[1-8]. Sodium paratungstate ($Na_6W_7O_{24}$)[1,2,5,6], anhydrous sodium carbonate[2], or a mixture consisting of 2 parts of lead oxide (PbO) and 1 part of lead chromate ($PbCrO_4$)[8] have been recommended as fluxes for the above minerals. Sodium paratungstate should first be pre-ignited at 800°C, and stored in a tightly-sealed bottle in a dessicator. Lead oxide and lead chromate should be pre-ignited separately at 800°C in platinum dishes, then combined, ground, and stored in a tightly-sealed bottle in a dessicator. Neither lead oxide nor lead chromate attack platinum at the specified temperature, but a mixture of the two attacks it severely[8]. Sodium paratungstate retains sulphur trioxide[2,3], and the lead oxide-lead chromate mixture retains sulphur oxides, chlorine, and fluorine[8]. Platinum boats should be employed if sodium paratungstate or sodium carbonate are used as the flux material.

13. The calcium and lead oxide flux mixture cannot adequately retain the oxides of sulphur or acidic sulphur compounds formed during the combustion of samples containing relatively large amounts of sulphide minerals (e.g., ores and mill products). Samples of high sulphur content can be analyzed if the exit end of the combustion tube is packed with a mixture of lead oxides (PbO and PbO_2) heated to 300-350°C[3], or with granular lead chromate heated to 300-400°C[7].

14. To determine whether all of the water has been expelled, examine the exit end of the combustion tube, the glass tube L, and the inlet tube of the water-absorption bulb. If moisture is present in any of the above parts of the apparatus, heating of the sample should be continued. Heating should not be stopped until the inlet tube of the water-absorption bulb has been free of moisture for at least 10 minutes. Usually all of the water is expelled after the sample has been heated for approximately 30 minutes.

Calculations

% Moisture (H_2O^-)

$$= \frac{L}{\text{Sample weight (g)}} \times 100$$

where:

L = loss in weight (g) of the sample after drying at 105-110°C.

$$\% \text{ Total water} = \frac{I_S - I_B}{\text{Sample weight (g)}} \times 100$$

where:

I_S = increase in weight (g) of the water-absorption bulb for the sample.

I_B = increase in weight (g) of the water-absorption bulb for the blank.

$$\% \text{ Combined water } (H_2O^+) = \% \text{ total water} - \% \text{ moisture}.$$

References

1. A.W. Groves, "Silicate Analysis", 2nd ed., George Allen and Unwin Ltd., London, pp 94-102, 269-274 (1951).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 814-835 (1953).

3. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 299-304, 752-754 (1948).

4. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 115-116, 217-223, 303, 323, 426-430, 487 (1968).

5. J.P. Riley, Analyst, 83, 42 (1958).

6. J.P. Riley and H.P. Williams, Mikrochim. Acta, 525 (1959).

7. P.G. Jeffery and A.D. Wilson, Analyst, 85, 749 (1960).

8. L.C. Peck, "Systematic Analysis of Silicates", U.S. Geol. Surv. Bull., 1170, pp 17-21, 83 (1964).

DETERMINATION OF NICKEL IN ORES AND MILL PRODUCTS BY PRECIPITATION WITH DIMETHYLGLYOXIME

Principle

Nickel is determined by weighing as the red dimethylglyoximate [$Ni(C_4H_7O_2N_2)_2$] after precipitation with dimethylglyoxime from a weakly ammoniacal medium[1-3].

Outline

The sample is decomposed with hydrochloric and nitric acids. The solution is evaporated to dryness to remove excess nitric acid, and acid-insoluble material is ultimately removed by filtration.

If iron is present and cobalt is absent, copper, bismuth, palladium, and various other elements of the copper and arsenic groups (molybdenum, rhenium, silver, platinum metals, gold, cadmium, mercury, germanium, tin, lead, arsenic, antimony, selenium, and tellurium) are precipitated as the sulphides from a dilute hydrochloric acid medium and separated from nickel by filtration. The nickel in the filtrate is ultimately precipitated with dimethylglyoxime from an ammoniacal ammonium chloride-sodium citrate medium, and the precipitate is separated by filtration, dried, and weighed.

If both iron and cobalt are present, iron is separated from nickel and cobalt by chloroform extraction of its cupferron complex from a dilute hydrochloric acid medium. The copper and arsenic group elements in the aqueous phase are subsequently separated as the sulphides. The nickel in the resulting filtrate is ultimately precipitated with dimethylglyoxime.

Discussion of interferences

Interference from copper, bismuth, and palladium, which form soluble and insoluble dimethylglyoxime compounds that co-precipitate with, or are occluded by nickel dimethylglyoximate[1,3], is avoided by separating these elements from nickel by precipitation as the sulphides with hydrogen sulphide from an approximately 0.5 M hydrochloric acid medium[4]. Tungsten is only partly removed by this separation procedure, but several mg do not interfere in the determination of nickel[1].

Iron (II), which is formed during the hydrogen sulphide separation procedure and which interferes by forming a soluble red complex with dimethylglyoxime in ammoniacal media, is reoxidized to the trivalent state with bromine, prior to the precipitation of nickel[1]. Interference from iron (III) and other elements that form hydrous oxides in ammoniacal media [e.g., aluminum, chromium (III), manganese, magnesium, and the alkaline earths] is avoided by complexing these elements with ammonium chloride and sodium citrate, prior to the precipitation of nickel.

Cobalt (II), in the absence of iron (III), forms a soluble brown dimethylglyoxime compound that is readily removed from the nickel precipitate by washing the precipitate with water[3]. Up to approximately 100 mg of cobalt do not interfere if sufficient dimethylglyoxime is added to combine with both the cobalt and the nickel[5]. In the presence of iron (III), cobalt interferes because it forms a mixed reddish-brown cobalt-iron-dimethylglyoxime compound ($FeCoC_{12}H_{19}N_6O_6$) that cannot be removed by washing[3]. This interference can be eliminated by separating iron from cobalt and nickel by chloroform extraction of its cupferrate from a hydrochloric acid medium.

Moderate amounts of vanadium, and several mg of silica do not interfere[1-3].

Range

The method is suitable for samples containing approximately 0.5 to 20% of nickel, but material containing higher concentrations can also be analyzed if the initial sample solution is diluted to a definite volume with water and a suitable aliquot is taken.

Reagents

Dimethylglyoxime solution, 1% w/v in ethyl alcohol.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% hydrochloric acid saturated with hydrogen sulphide.

Bromine water. Water saturated with bromine.

Cupferron solution, 9% w/v. Prepare fresh as required.

Sulphuric acid, 50% v/v.

Chloroform. Analytical reagent-grade.

Procedures

Iron present and cobalt absent

Transfer 0.2-1 g of powdered sample, containing approximately 5-40 mg of nickel (Note 1), to a 250-ml beaker, add 10 ml each of water and concentrated hydrochloric acid, cover the beaker, and boil for several minutes. Add 10 ml of concentrated nitric acid, boil until the decomposition of acid-soluble material is complete, then remove the cover and evaporate the solution to dryness. Wash down the sides of the beaker with approximately 10 ml of concentrated hydrochloric acid, evaporate the solution to dryness again, then add 7 ml of concentrated hydrochloric acid and approximately 25 ml of water, and heat gently to dissolve the soluble salts. Filter the resulting solution (Whatman No. 30 paper) into a 400-ml beaker, using paper pulp, if necessary, and wash the beaker, paper, and residue (Note 2) with hot water.

Dilute the filtrate to approximately 150 ml with hot water, and pass hydrogen sulphide through the solution for approximately 10 minutes to precipitate the copper and arsenic group elements. Filter the solution (Whatman No. 32 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hydrogen sulphide wash solution. Discard the paper and precipitate. Boil the filtrate to expel hydrogen sulphide, and add 5-10 ml of bromine water to oxidize iron (II). Cover the beaker, boil the solution for 5 minutes, then remove the cover and continue boiling until all of the bromine has been expelled. Filter the solution if it is not perfectly clear, and add 2 g of ammonium chloride and 3 g of sodium citrate or citric acid.

Using litmus paper, neutralize the resulting solution with concentrated ammonium hydroxide. Add several drops in excess (Note 3), then add concentrated hydrochloric acid, by drops, until the solution is just acid, and add several drops in excess. Heat the solution to 60-80°C, and add at least 5 ml of 1% dimethylglyoxime solution for each 10 mg of nickel present (Note 4). Stir the solution, and add concentrated ammonium hydroxide, by drops, until the solution is distinctly alkaline to litmus paper. Stir thoroughly, and allow the solution to stand in a warm place for 1 hour, or up to 12 hours if the amount of nickel dimethylglyoximate precipitate is small. Cool, filter the solution through a tared, sintered-glass, medium-porosity filtering crucible, using suction, and test the filtrate for completeness of precipitation by adding several ml of dimethylglyoxime solution. Transfer the precipitate quantitatively to the crucible and wash the crucible and precipitate thoroughly with cold water (Note 5). Dry the precipitate for 1 hour at 110-120°C, cool in a dessicator and weigh. Repeat the drying and weighing until constant weight is obtained.

Both iron and cobalt present

Decompose 0.2-1 g of sample, containing not more than 100 mg of cobalt (Note 6), by the method described above. After evaporation of the solution to dryness to remove nitric acid, dissolution of the residue in dilute hydrochloric acid, and filtration of the solution to remove acid-insoluble material (Note 2), add 8 ml of concentrated hydrochloric acid, and transfer the resulting solution to a 250-ml separatory funnel. Dilute to approximately 150 ml with water, and cool the solution to 10-15°C in an ice-bath. Add sufficient cold 9% cupferron solution to precipitate the iron, mix, stopper, and extract the reddish-brown iron cupferrate by repeated shaking, for 1 minute each time, with 25-ml portions of chloroform until the organic layer is colourless (Note 7). Discard each extract. Transfer the aqueous phase to a 400-ml beaker, warm gently to remove residual chloroform, then evaporate the solution to approximately 50 ml. Add 15 ml of 50% sulphuric acid and 10 ml of concentrated nitric acid, cover the beaker, and boil the solution for 20-30 minutes to destroy organic material. Cool, remove the cover, and evaporate the solution to fumes of sulphur trioxide. If organic material is still present, repeat the treatment with nitric acid and evaporate the solution to dryness. Add 7 ml of concentrated hydrochloric acid and approximately 25 ml of water, and heat to dissolve the salts. Dilute the solution to 150 ml with hot water, and proceed with the hydrogen sulphide separation of the copper and arsenic group elements, the precipitation of nickel dimethylglyoximate (Note 8), and the subsequent treatment of the precipitate as described above.

Notes

1. More than approximately 40 mg of nickel cannot be conveniently handled by this method because of the bulkiness of the nickel dimethylglyoximate precipitate.

2. If an appreciable amount of acid-insoluble material (i.e., silicates) is present, proceed as follows:

Transfer the residue quantitatively to the filter paper, and transfer the paper and contents to a 30-ml platinum crucible. Burn off the paper at a low temperature and ignite at approximately 750°C. Cool the crucible, add 1 ml of 50% sulphuric acid and 3-5 ml of concentrated hydrofluoric acid, heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid. Fuse the residue with 1 g of sodium carbonate, cool, and transfer the crucible and contents to the beaker containing the initial filtrate. When dissolution of the melt is complete, remove the crucible after washing it thoroughly with hot water, boil the resulting solution for several minutes to expel carbon dioxide, then proceed as described.

If only a small amount of light-coloured residue is present, it may be discarded.

3. If the solution is cloudy at this stage, acidify it with concentrated hydrochloric acid, and add sufficient additional sodium citrate and/or ammonium chloride, as required, so that a clear solution is obtained on re-neutralization of the solution with concentrated ammonium hydroxide.

4. Theoretically 4 ml of 1% dimethylglyoxime solution are required for each 10 mg of nickel, but a moderate excess is advisable. Excess dimethylglyoxime has no adverse effect unless the reagent itself crystallizes out of solution[3].

5. To avoid loss of nickel because of the solubility of nickel dimethylglyoximate in hot aqueous solutions, the sample solution should be cooled before filtration, and cold water should be employed to wash the precipitate[3].

6. Larger amounts of cobalt inhibit the precipitation of nickel dimethylglyoximate from ammoniacal solutions (Note 8)[3].

7. Approximately 2-2.5 ml of 9% cupferron solution are usually sufficient for the complexation of 10 mg of metal ion. To test for completeness of precipitation, extract the solution twice with chloroform, then add 1-2 ml of cupferron solution. Complete precipitation is indicated by a transient white precipitate resulting from the presence of excess cupferron.

8. Sufficient dimethylglyoxime must be added to react with the cobalt and to provide an excess for the nickel. If the sample solution contains a large amount of cobalt, care should be taken that the alcohol content of the solution, resulting from the addition of the dimethylglyoxime solution, does not exceed 50% by volume. Nickel dimethylglyoximate is increasingly soluble in solutions containing greater proportions of alcohol[1].

Calculations

% Ni

$$= \frac{0.2031 \times \text{Weight of dried precipitate (g)}}{\text{Sample weight (g)}}$$

x 100

Other applications

With modifications in the decomposition and separation procedures, this method can be employed to determine nickel in minerals, iron, steel, and ferrous alloys[3].

References

1. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 404-411 (1953).

2. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 2, pp 404-406 (1962).

3. H. Diehl, "The Applications of the Dioximes to Analytical Chemistry", G. Frederick Smith Chemical Co., Columbus, Ohio, pp 23-33 (1940).

4. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, 54 (1938).

5. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, 619 (1939).

DETERMINATION OF SILICA IN IRON, MANGANESE, TITANIUM AND SULPHIDE ORES AND MILL PRODUCTS, REFRACTORY AND ACID-SOLUBLE SILICATE ROCKS AND MINERALS, CARBONATE ROCKS, CLAY, AND SHALE BY THE CLASSICAL METHOD

Principle

Silica is determined from the loss in weight of the impure silica precipitate obtained by acid dehydration, after ignition of the precipitate and subsequent volatilization of silicon as the tetrafluoride from a hydrofluoric-sulphuric acid medium[1-5].

Outline

Iron, manganese and sulphide ores and mill products, containing 0.25% or less of fluoride, are decomposed with hydrochloric, nitric, and perchloric acids, and the solution is evaporated to fumes of perchloric acid to dehydrate the silica. Silica and other acid-insoluble material is ultimately separated by filtration, ignited, and fused with sodium carbonate. The melt is dissolved in the initial filtrate, and silica is again dehydrated and separated by filtration. The residual silica in the filtrate is recovered by dehydration, and the impure precipitates are combined, ignited, and weighed. The resultant residue is treated with hydrofluoric and sulphuric acids and the solution is evaporated to dryness to volatilize silicon as the tetrafluoride, and to remove excess sulphuric acid. The resulting non-volatile residue, containing the occluded impurities, is ignited and weighed.

> Samples containing more than 0.25% of fluoride are decomposed with hydrochloric and nitric acids in the presence of aluminum chloride, and the solution is evaporated to dryness to dehydrate the silica. Silica is ultimately determined as described above, after dehydration with hydrochloric acid.

Titanium ores and mill products are decomposed by fusion with potassium pyrosulphate. The melt is dissolved in dilute sulphuric acid and the solution is evaporated to fumes of sulphur trioxide to dehydrate the silica. Silica is subsequently determined as described above, after recovery of the residual silica in the initial filtrate by dehydration with sulphuric acid.

Refractory and acid-soluble silicate rocks and minerals, clay, and shale are decomposed by fusion with sodium carbonate. The melt, depending on the fluoride content, is dissolved in either dilute perchloric acid or in dilute hydrochloric acid containing aluminum chloride. Silica is subsequently determined, after dehydration with perchloric or hydrochloric acid, by the respective methods described for iron, manganese and sulphide ores and mill products.

Carbonate rocks, depending on the fluoride content, are decomposed and analyzed for silica by the appropriate methods described for iron, manganese and sulphide ores and mill products.

Discussion of interferences

Various elements, depending on the acid employed for the dehydration of the polymerized silicic acid, contaminate the silica precipitate because they form insoluble compounds during the dehydration procedure, or because they are retained by the precipitate. Regardless of whether perchloric, sulphuric, or hydrochloric acid is employed for dehydration, niobium, tantalum, and tungsten form insoluble hydrous oxides that co-precipitate with silica. Boron is partially co-precipitated, small amounts of aluminum and iron are retained by the precipitate, and tin, antimony, and bismuth may be co-precipitated or retained, to some extent, by the precipitate[2-5]. Titanium and zirconium are not appreciably co-precipitated in the absence of phosphate unless the solution is diluted to such an extent, prior to filtration of the silica, that hydrolysis of these elements occurs. In the presence of moderate amounts of phosphate, titanium and zirconium are co-precipitated as insoluble phosphates[3]. Molybdenum, germanium, and vanadium may be partly precipitated during dehydration of silica with perchloric acid[2]. Manganese may precipitate as the dioxide, but this compound can readily be dissolved (i.e., reduced) and prevented from contaminating the silica precipitate by the addition of sodium nitrite[1]. During dehydration of silica with hydrochloric acid, silver and lead form insoluble chlorides, gold and palladium are partly precipitated as the elements, and arsenic (III) and germanium are volatilized as the chlorides. Lead, barium, and calcium form insoluble sulphates, and germanium may co-precipitate during dehydration with sulphuric acid[2].

More than approximately 0.25% of fluoride causes low results for silica, particularly in the absence of aluminum, because of the loss of silicon as the volatile tetrafluoride during the sample decomposition and/or dehydration steps[2-4]. Interference from fluoride is eliminated by complexing it with aluminum during sample decomposition with hydrochloric and nitric acids, or before dehydration of silica with hydrochloric acid following sample decomposition by fusion[6].

Positive error from most of the compounds that contaminate the silica precipitate is avoided by treating the impure silica residue, obtained after ignition and conversion of the silica and impurities to anhydrous oxides, with hydrofluoric and sulphuric acids. Silica is volatilized as the tetrafluoride, and the interfering impurities are converted to sulphates and subsequently re-converted to oxides during ignition of the non-volatile residue. The presence of sulphuric acid during the volatilization of silica eliminates positive error from titanium and other impurities that form volatile fluorides (e.g., niobium, tantalum, and zirconium)[3,5]. Positive error from tungsten, which volatilizes as the trioxide at high temperatures, can be avoided by igniting both the impure silica precipitate and the non-volatile residue obtained after the volatilization of the silicon, at temperatures below 850°C[3,4].

Boron and arsenic (III), if present in the impure silica precipitate, cause high results for silica because they also volatilize as fluorides during the hydrofluoric-sulphuric acid treatment of the ignited precipitate[2-4].

Phosphate may cause positive error resulting from the expulsion of phosphoric acid[3].

Tin, antimony, arsenic, and other elements that are readily reduced to the metallic state by carbon from the filter paper (e.g., lead, silver, gold, bismuth, and palladium) during the ignition of the impure silica precipitate will alloy with the platinum crucible, and may cause error in the silica result because of indefinite changes in the weight of the crucible after the first and second ignitions. Interference from tin, antimony, and arsenic can be eliminated, during dehydration of silica with perchloric or sulphuric acid, by volatilizing these elements as the bromides with hydrobromic acid.

Insufficient washing of the silica precipitate, particularly when sodium or potassium salts are employed for fusion of the sample or acid-insoluble residue, usually causes a negative error in the silica result. Alkali salts that contaminate the impure silica precipitate cause low results for silica because they volatilize, in part, during ignition of the precipitate, and because the remainder decomposes and reacts with the silica to form an alkali silicate and a volatile acid. The resultant silicate is decomposed during the hydrofluoric-sulphuric acid treatment of the impure silica residue, and the alkali metal is subsequently weighed as the sulphate rather than the lighter oxide. Any alkali metal that is initially present as the chloride in the impure precipitate, and that is not decomposed or volatilized during ignition of the precipitate, also causes low results for silica because it is weighed first as the chloride, then as the heavier sulphate. High results will be obtained if the non-volatile residue obtained after the hydrofluoric-sulphuric acid treatment is ignited at a temperature high enough to volatilize all of the resultant alkali sulphate. Lead, calcium, strontium, and barium sulphates also cause low results for silica because of the formation of silicates during ignition of the silica precipitate[3].

If un-decomposed material containing silicates is present in the ignited impure silica residue, incorrect results, caused by subsequent weight changes, will be obtained for silica even though all of the silicon in the un-decomposed portion is volatilized during the hydrofluoric-sulphuric acid treatment. For example, if the undecomposed material is microcline ($KAlSi_3O_8$), the non-volatile residue remaining after the volatilization of silicon and the subsequent ignition will consist of potassium sulphate and aluminum oxide instead of potassium oxide and aluminum oxide[3].

Range

The method is suitable for samples containing more than approximately 0.5% of silica.

Reagents

Sulphuric acid, 50%, 10%, and 5% v/v.

Hydrochloric acid wash solutions, 5%, 2%, and 1% v/v.

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Iron, manganese and sulphide ores and mill products

(a) Fluoride content 0.25% or less

Transfer 0.5-2 g of powdered sample (Note 1), depending on the expected silica content, to a 400-ml beaker, moisten with several ml of water, and add 30 ml of concentrated hydrochloric acid. Cover the beaker, and heat gently until the decomposition of acid-soluble material is complete, then add 5 ml of concentrated nitric acid and heat gently for approximately 5 minutes. Cool, add 25 ml of concentrated perchloric acid, evaporate the solution to fumes of perchloric acid (Note 2), and continue fuming for 10-15 minutes (Note 3). Cool, remove the cover, add 50 ml of water and, if necessary, several crystals of sodium nitrite to reduce any manganese dioxide present. Heat gently to dissolve the soluble salts, filter the solution (Whatman No. 541 paper) into a 600-ml beaker, and transfer the silica and acid-insoluble residue quantitatively to the filter paper. Wash the paper and residue 10 times with hot 2% hydrochloric acid, then 5-10 times with hot water to remove perchlorates (Note 4). If necessary, evaporate the filtrate to approximately 200 ml, transfer it to the original beaker (Note 5), and evaporate the solution to about 125 ml.

Transfer the paper and contents to a 30-ml platinum crucible (Note 6), burn off the paper at a low temperature in a muffle furnace, and ignite at approximately 800°C. Cool the crucible, add 3-5 g of sodium carbonate to the residue and mix thoroughly. Cover the crucible and fuse the mixture at 900-1000°C until a clear melt is obtained (Note 7). Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, allow the crucible and contents to cool, then transfer the crucible and cover to the beaker (covered) containing the initial filtrate. When dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with hot water. Add 10 ml of concentrated perchloric acid to the resulting solution, evaporate it to fumes of perchloric acid, cover the beaker, and continue fuming for 10-15 minutes. Cool, remove the cover, add 75 ml of water and, if necessary, several crystals of sodium nitrite to reduce manganese dioxide, and heat gently to dissolve the soluble salts. Filter the solution, transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate as described above. Transfer the paper and contents to the original platinum crucible (Note 6).

If necessary, evaporate the filtrate to approximately 200 ml, transfer it to the original beaker, and add 10 ml of concentrated perchloric acid. Repeat the evaporation to fumes of perchloric acid and the subsequent filtration (Note 8) and washing of the paper and precipitate as described above (Note 9). Add the paper containing the residual silica precipitate to the platinum crucible containing the initial precipitate, and burn off the paper at a low temperature in a muffle furnace (Note 10). Ignite the combined precipitates at approximately 1150°C (Notes 11 and 12) for 30 minutes, cool in a dessicator and weigh (Note 13). Repeat the ignition and weighing until constant weight is obtained, then moisten the residue in the crucible with several drops of water. Add 4 or 5 drops of 50% sulphuric acid and 10 ml of concentrated hydrofluoric acid, and slowly evaporate the solution to dryness to volatilize the silica and to remove excess sulphuric acid (Notes 14 and 15). Ignite the residue at 1150°C (Note 11) for 5 minutes, cool in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained, and correct the result obtained for the sample by subtracting that obtained for the reagent blank (Note 16).

(b) Fluoride content greater than 0.25%

Add 4.5 g of aluminum chloride hexahydrate to 0.5-2 g of sample (Notes 1 and 17), and decompose the sample with concentrated hydrochloric and nitric acids as described above. Evaporate the solution to complete dryness in a hot water-bath (Note 18). Cool, wash down the sides of the beaker with 10-15 ml of concentrated hydrochloric acid, and evaporate the solution to dryness in the water-bath again to remove nitric acid. Cool, add 10 ml of concentrated hydrochloric acid to the residue, warm gently for 1-2 minutes (Note 19), then add 50 ml of water, place the beaker in the hot water-bath, and stir to dissolve the soluble salts. Filter the solution (Whatman No. 541 paper) into a 600-ml beaker, transfer the silica and acid-insoluble residue quantitatively to the filter paper, and wash the paper and residue 5-7 times with hot 5% hydrochloric acid followed by hot water. If necessary, evaporate the filtrate to approximately 200 ml, transfer it to the original beaker (Note 5), and evaporate the solution to about 125 ml.

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper, and ignite and fuse the residue with sodium carbonate as described above. Dissolve the melt in the initial filtrate, and remove the crucible and cover after washing them thoroughly with hot water. Evaporate the solution to approximately 50 ml, then place the beaker in a hot water-bath and evaporate the solution to complete dryness. Cool, add 10 ml of concentrated hydrochloric acid to the residue, warm gently for 1-2 minutes, then add 75 ml of water, place the beaker in a hot water-bath, and stir to dissolve the salts. As soon as the dissolution of the soluble salts is complete (Note 20), filter the solution and transfer the precipitate quantitatively to the filter paper. Wash the paper and precipitate as described above, and transfer the paper and contents to the original platinum crucible (Note 6).

If necessary, concentrate the filtrate by evaporation, transfer it to the original beaker, evaporate the solution to dryness, and bake the residue in an oven at approximately 105°C for 1 hour (Note 21). Cool, add 10 ml of concentrated hydrochloric acid and 75 ml of water, and dissolve the salts as described above. Filter the solution (Note 8), transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate with cold 1% hydrochloric acid and hot water. Add the paper containing the residual silica precipitate to the platinum crucible containing the initial precipitate (Notes 6 and 9), burn off the paper at a low temperature, then proceed with the ignition and weighing of the crucible and combined precipitates, the volatilization of silica, and the subsequent ignition and weighing of the crucible and non-volatile residue as described above.

B - Titanium ores and mill products

Transfer 0.5 g of powdered sample (Note 22) to a 30-ml platinum crucible, add 7 g of potassium pyrosulphate, mix, and fuse the mixture over an open flame for approximately 30 minutes. Cool, transfer the crucible and contents to a 400-ml beaker, and add 100 ml of 10% sulphuric acid. Heat gently to dissolve the melt, then remove the crucible after washing it thoroughly with 10% sulphuric acid (Note 23). Add 40 ml of 50% sulphuric acid, evaporate the solution to fumes of sulphur trioxide, and continue fuming for 2-4 minutes. Cool, carefully add approximately 180 ml of water in small portions, and stir to dissolve the soluble salts. Filter the solution into a 600-ml beaker, transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate thoroughly with 5% sulphuric acid followed by hot water to remove potassium salts. Transfer the paper and contents to the original platinum crucible (Note 6).

If necessary, concentrate the filtrate by evaporation, transfer it to the original beaker, and repeat the evaporation to fumes of sulphur trioxide and the subsequent filtration (Note 8) and washing of the precipitate as described above. Add the paper containing the residual silica precipitate to the platinum crucible containing the initial precipitate (Notes 6 and 9), burn off the paper at a low temperature, and proceed with the ignition and subsequent treatment of the combined precipitates as described in Procedure A (a).

C - Refractory and acid-soluble silicate rocks and minerals, clay, and shale

(a) Fluoride content 2% or less

Transfer 0.5-1 g of powdered sample (Note 24) to a 30-ml platinum crucible, and ignite in an electric muffle furnace at 800-900°C for approximately 30 minutes (Note 25). Cool the crucible, add a five-fold weight excess of sodium carbonate, mix, and cover the mixture with 0.5-1 g of sodium carbonate. Cover the crucible with a platinum cover, heat at a low temperature for 5-10 minutes, then fuse the mixture (Note 7) at 900-1000°C for approximately 30 minutes. Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, allow the crucible and contents to cool, then transfer the crucible and cover to a 400-ml (covered) beaker containing 70 ml of water and 30 ml of concentrated perchloric acid. When dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with hot water (Note 26). Evaporate the resulting solution to fumes of perchloric acid, cover the beaker, and continue fuming for 10-15 minutes (Note 3). Cool, remove the cover, add approximately 100 ml of water and, if necessary, several crystals of sodium nitrite to reduce any manganese dioxide present, and heat gently to dissolve the soluble salts. Filter the solution, transfer the precipitate quantitatively to the filter paper, and wash the paper and silica precipitate with hot 2% hydrochloric acid and hot water as described in Procedure A (a).

Transfer the paper and precipitate to the original platinum crucible, then proceed with the evaporation of the filtrate, the recovery of the residual silica (Note 27), and the ignition and subsequent treatment of the combined silica precipitates (Note 28) as described in Procedure A (a).

(b) Fluoride content greater than 2%

Following sample decomposition by fusion with sodium carbonate as described above, transfer the crucible and cover to a 400-ml beaker containing 4.5 g of aluminum chloride hexahydrate dissolved in 75 ml of water. Cover the beaker, and add several drops of ethyl alcohol (Note 29) and 25 ml of concentrated hydrochloric acid. When dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with hot water (Note 26), evaporate the resulting solution to approximately 50 ml, then place the beaker in a hot water-bath and evaporate the solution to complete dryness. Cool, add 10 ml of concentrated hydrochloric acid to the residue and warm gently for 1-2 minutes (Note 19). Add 75 ml of water, place the beaker in the hot water-bath, and stir to dissolve the salts. As soon as the dissolution of the soluble salts is complete (Note 20), filter the solution, transfer the precipitate quantitatively to the filter paper, and wash the paper and silica precipitate with hot 5% hydrochloric acid and hot water as described in Procedure A (b). Transfer the paper and precipitate to the original platinum crucible, then proceed with the evaporation of the filtrate, the recovery of the residual silica, and the ignition and subsequent treatment of the combined silica precipitates as described in Procedure A (b).

D - Carbonate rocks

Depending on the absence or presence of fluoride ion, decompose 0.5-1 g of powdered sample (Note 30) and determine silica by the method described in Procedure A (a) or A (b), respectively (Note 31).

Notes

1. This procedure is not applicable to lead sulphide ores, or to other sulphide ores in which an appreciable amount of lead sulphate is initially present in the sample, or is formed during the decomposition procedure.

2. If the sample contains an appreciable amount of tin, arsenic, and/or antimony, proceed as follows:

Dilute the solution to approximately 40 ml with water, add 5-10 ml of concentrated hydrobromic acid, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, repeat the hydrobromic acid treatment and subsequent evaporation to fumes of perchloric acid, then proceed as described.

3. The solution should be heated just vigorously enough so that the perchloric acid refluxes down the sides of the beaker. If an appreciable amount of perchloric acid has inadvertently been removed during the initial evaporation of the solution to fumes, more should be added at this stage. Care should be taken that the contents of the beaker do not become solid during the fuming stage. The separation of silica is always incomplete if this occurs[2].

4. Deflagration and consequent loss of silica may occur during the subsequent ignition if the residue is not washed free of perchlorates.

5. The transfer of the filtrate to the original beaker ensures the subsequent recovery of small amounts of silica that may have been retained in the beaker during the filtration step.

6. To ensure the recovery of any silica that may have adhered to the inside of the funnel during the filtration step, wipe the top inner part of the funnel with a small moistened piece of filter paper, and add the paper to the platinum crucible.

7. Oxidizing conditions must be maintained during fusions with sodium carbonate or else iron and easily reducible elements (e.g., lead and zinc) will alloy with the platinum crucible. If a flame is employed for fusion, the sample should be heated gradually to avoid loss by spattering, the flame should not be allowed to envelop the crucible completely, and the bottom of the crucible should never be allowed to come into contact with the blue cone of the burner flame. Flame fusions generally result in some loss of iron from the sample material to the platinum crucible. The presence of an oxidizing atmosphere during fusion can be ensured by employing a muffle furnace, started cold, or at a temperature below 500°C, followed by gradual heating to the desired temperature[2].

8. The addition of a small amount of ashless paper pulp to the solution prior to filtration will aid in collecting the small residual silica precipitate.

9. To ensure the recovery of any silica that may have adhered to the inner rim of the beaker during the filtration step, wipe the top inner part of the beaker with a small piece of moistened filter paper, and add the paper to the platinum crucible containing the initial silica precipitate.

10. The paper should be burned off at as low a temperature as possible to avoid the formation of black silicon carbide. High results are obtained for silica in the presence of this compound because the hydrofluoric acid, employed for the subsequent volatilization of the silica, decomposes the carbide, and the resultant carbon is burned and eliminated as carbon dioxide during the final ignition of the non-volatile material[2].

11. If the sample contains tungsten, the ignition of the residue should be conducted at a temperature below 850°C to prevent the volatilization of tungsten trioxide[3,4].

12. Care must be taken during ignition to prevent mechanical loss of the light, fluffy, silica residue.

13. Because the finely-divided ignited silica precipitate is hygroscopic, the crucible and residue should be weighed as soon as they are cool to avoid error resulting from the absorption of water.

14. In exact work, the hydrofluoric-sulphuric acid treatment of the impure silica residue should be repeated to ensure that all of the silica present has been volatilized as silicon tetrafluoride.

15. If the residue is suspected to contain phosphates, the removal of the excess sulphuric acid by evaporation should be conducted at as low a temperature as possible to avoid error resulting from the expulsion of phosphoric acid[3].

16. In this procedure and the subsequent procedures, no account is taken of the small amount of soluble silica that remains in the filtrate and cannot be recovered by a third dehydration. The error in the silica result is relatively small. The amount of silica remaining in solution after two dehydrations may be more than compensated for by the introduction of silica from the reagents and from the glass vessels employed if a reagent blank is not carried through the procedure[5].

17. This procedure is not applicable to ores containing an appreciable amount of silver, gold, lead, or palladium.

18. Any crust, with liquid underneath, that forms during evaporation of the sample solution to dryness must be broken and the liquid stirred with a platinum or blunt pyrex rod. Incomplete evaporation to dryness will result in a very difficult filtration[2].

19. The residue containing the dehydrated silica and anhydrous chlorides should not be treated first with water. Iron and aluminum hydrolyze, to some extent, under these conditions, and form insoluble basic chlorides which will not dissolve completely on the subsequent addition of hydrochloric acid[4].

20. Because the amount of silica that reverts to the colloidal or soluble state in dilute hydrochloric acid solutions increases with time of heating, and with time of standing prior to filtration, the heating step to dissolve the soluble salts should not be prolonged unnecessarily, and the solution should subsequently be filtered without delay[5].

21. The dehydration of the residue should not be conducted at temperatures above 110°C because of the possible interaction, if magnesium is present, of magnesium chloride and silica to form soluble magnesium silicate. Prolonged heating results in increased contamination of the silica by foreign ions[4,5].

22. This procedure is not applicable to samples containing more than approximately 0.25% of fluoride.

23. If any quartz or un-decomposed silicate material is present at this stage, proceed as follows:

Filter the solution (Whatman No. 541 paper), transfer the residue quantitatively to the filter paper, and wash the paper and residue with 10% sulphuric acid. Transfer the paper and contents to a 30-ml platinum crucible and burn off the paper at a low temperature. Ignite and fuse the residue with 1-2 g of sodium carbonate and dissolve the melt in the initial filtrate as described in Procedure A (a), then proceed as described.

24. Because silicate rocks and minerals, clay and shale contain an appreciable amount of aluminum, silica can be determined in these materials in the presence of considerably greater amounts of fluoride than in ore samples of low aluminum content[2,6].

25. Ignition of the sample oxidizes any reducing substances (e.g., carbonaceous material and pyrite) which could attack the platinum crucible during the subsequent fusion procedure.

26. If more than a few grains of undecomposed material are visible or detectable as a gritty residue with a stirring rod, the sample should be discarded and the fusion should be repeated at a higher temperature.

27. The filtrate can be used for the determination of aluminum, calcium, and magnesium by the Gravimetric-Ammonium Hydroxide (Procedure C, p 145), the Volumetric-Oxalate (p 243), and the Gravimetric-Pyrophosphate (p 182) Methods, respectively. The filtrate from the reagent blank solution should be retained for use as a blank in the determination of aluminum.

28. With samples of high silica content, the error in the silica determination (Note 16) at approximately the 40 to 75% level is about 0.2% . In classical silicate analysis, the customary method of recovering the small amount of soluble silica that remains in the filtrate after the second dehydration involves occlusion of the silica with the mixed hydrous oxide (R_2O_3) precipitate of iron, aluminum, and other elements (e.g., titanium and phosphorus) obtained by treatment of the filtrate with ammonium hydroxide. The residual occluded silica is subsequently determined by basically the same method as that described in Procedure B, after ignition and fusion of the mixed hydrous oxides with potassium pyrosulphate. The reliability of the above method is questionable because not all of the silica remaining in solution is occluded by the mixed hydrous oxide precipitate, and because it essentially involves recovery of the residual silica by a third dehydration[2,5,6]. If an exact analysis is desired, the residual silica should preferably be determined in the filtrate obtained after either the first or the second dehydration by a suitable spectrophotometric method[2,7].

29. The addition of a small amount of alcohol, prior to the dissolution of the melt with hydrochloric acid, is recommended to reduce any manganese (VI) present to the divalent state. This prevents attack on the platinum crucible, during dissolution of the melt, by free chlorine which is produced by the reaction of manganate ion with hydrochloric acid[4].

30. To avoid loss of sample resulting from the rapid reaction between carbonates and acid, moisten the sample with approximately 10 ml of water, cover the beaker, and slowly add 10 ml of concentrated hydrochloric acid in small portions. When the decomposition of the carbonates is complete, proceed as described.

31. If Procedure A (a) is employed, the filtrate obtained after the recovery of the residual silica can be used for the determination of aluminum, calcium, and magnesium by the Gravimetric-Ammonium Hydroxide (Procedure D, p 145), the Volumetric-Oxalate (p 243), and the Gravimetric-Pyrophosphate (p 182) Methods, respectively. The filtrate from the reagent blank solution should be retained for use as a blank in the determination of aluminum.

Calculations

$$\%SiO_2 = \frac{L_S - L_B}{\text{Sample weight (g)}} \times 100$$

where:

L_S = loss in weight (g) of the ignited impure silica residue after treatment with hydrofluoric and sulphuric acids.

L_B = loss in weight (g) of the blank residue after treatment with hydrofluoric and sulphuric acids.

Other applications

The method described in Procedure A (a) can be employed to determine silica in steel, steel slags, metals, alloys, and cement. It can also be applied to chromium ores and mill products after the removal of chromium by volatilization as chromyl chloride. The methods described in Procedures C (a) and (b) are applicable to sandstone, silica sand, quartzite, silicon carbide, bauxite, magnesite, fire-brick, and boron-free glass[4].

References

1. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E247-71, pp 745-747 (1971).

2. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 2, pp 136-159 (1962).

3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 671-682 (1953).

4. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 950-960, 966-972, 1115 (1962).

5. I.M. Kolthoff and E.B. Sandell. "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 398-409, 738-739 (1948).

6. H.R. Shell, Anal. Chem., 27, 2006 (1955).

7. P.G. Jeffery and A.D. Wilson, Analyst, 85, 478 (1960).

DETERMINATION OF SILICA IN SILICA SAND, SANDSTONE, AND QUARTZITE BY VOLATILIZATION AS SILICON TETRAFLUORIDE (INDIRECT RAPID CONTROL METHOD)

Principle

Silica is determined from the loss in weight of the sample, after ignition and subsequent volatilization of the silica as silicon tetrafluoride from a hydrofluoric-perchloric acid medium[1,2].

Outline

The sample is ignited at approximately 1150°C to remove water, to oxidize carbonaceous material, and to convert any sulphides or carbonates present to oxides. The ignited sample is weighed, and treated with hydrofluoric and perchloric acids to volatilize silica as silicon tetrafluoride and to convert the resulting non-volatile fluorides (sodium, potassium calcium, magnesium, aluminum, and iron) to perchlorates, respectively. The solution is ultimately evaporated to dryness and the resultant residue is re-ignited at 1150°C to convert the perchlorates to oxides, and weighed.

Discussion of interferences

Alkali metal chlorides, if present, are not decomposed to oxides or volatilized during the initial ignition step, and will cause low results for silica because of their conversion to perchlorates during the volatilization of silica, and subsequent conversion to the heavier oxides during the ignition of the non-volatile residue. Alkali metal and alkaline earth phosphates and sulphates may cause high results for silica if they remain unchanged in composition during the first ignition, but are partly or completely converted to lighter oxides during the second ignition[1].

Range

The method is suitable for highly siliceous sample materials containing more than approximately 98% of silica.

Procedure

Transfer 1 g of powdered sample to a 100-ml platinum dish, ignite at approximately 1150°C in a muffle furnace for about 15 minutes, cool in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained, then add 20 ml of concentrated hydrofluoric acid and allow the mixture to digest at room temperature for 1-2 hours or preferably overnight. Add 5 ml of concentrated perchloric acid and evaporate the resulting solution to fumes of perchloric acid. Cool, wash down the sides of the dish with water, and add 10 ml of concentrated hydrofluoric acid. Heat gently for 15-20 minutes, evaporate the solution to fumes of perchloric acid (Note 1), then to complete dryness. Ignite the residue at 1150°C for approximately 15 minutes, cool in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained.

Notes

1. If any un-decomposed material is visible or detectable as a gritty residue with a platinum rod, repeated treatment of the sample with hydrofluoric acid may be necessary to obtain complete decomposition of the silica and silicates.

Calculations

$$\%SiO_2 = \frac{L}{\text{Sample weight (g)}} \times 100$$

where:

L = loss in weight (g) of the pre-ignited sample after treatment with hydrofluoric and perchloric acids.

Other applications

This method can be employed to determine silica or silicon in silica refractories and elemental silicon, if nitric acid is used in the decomposition procedure[2].

References

1. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis" 2nd ed., John Wiley and Sons, Inc., New York, pp 851-852 (1953).

2. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 2, pp 155, 202 (1962).

DETERMINATION OF TOTAL SULPHUR IN ORES AND MILL PRODUCTS BY THE BARIUM SULPHATE METHOD

Principle

Sulphur is determined by weighing as barium sulphate, after conversion of elemental, sulphide, and other forms of sulphur to sulphate, and subsequent precipitation of the sulphate with barium chloride from a dilute hydrochloric acid medium$^{1-3}$.

Outline

Acid-soluble sulphide ores and mill products are treated with bromine-carbon tetrachloride or bromine-potassium bromide solution, followed by nitric acid, to oxidize elemental, sulphide, and other forms of sulphur to the sulphate form, and silica is ultimately dehydrated by evaporation with hydrochloric acid.

If lead, strontium, barium, chromium, and large amounts of calcium and iron are absent, the salts are dissolved in dilute hydrochloric acid, and silica and other acid-insoluble material is removed by filtration. The sulphide in the resulting filtrate is ultimately precipitated with barium chloride, and the precipitate is separated by filtration, ignited, and weighed. If the barium sulphate precipitate contains occluded molybdenum, the ignited precipitate is fused with sodium carbonate, the melt is digested in water, and the resultant barium carbonate precipitate is removed by filtration. The molybdenum in the filtrate is subsequently precipitated with alpha-benzoin oxime, and separated from sulphate by filtration. The sulphate in the resulting filtrate is ultimately re-precipitated.

If chromium and/or large amounts of iron are present and lead, strontium, barium, and/or large amounts of calcium are absent, chromium and iron are reduced to the trivalent and divalent states, respectively, with aluminum metal in a dilute hydrochloric-acid medium. The acid-insoluble material and excess aluminum are removed by filtration, and sulphate is precipitated from the resulting solution.

If lead, strontium, and/or large amounts of calcium are present and barium is absent, the hydrous oxides of iron, lead, and various other elements (aluminum, bismuth, tin, arsenic, antimony, titanium, and zirconium) are precipitated with ammonium hydroxide, and the solution is treated with ammonium carbonate to convert the insoluble lead, strontium, and calcium sulphates to insoluble carbonates and soluble sulphate. After filtration and dissolution of the precipitate, the mixed hydrous oxides and carbonates are re-precipitated to recover the occluded sulphate. The sulphate in the combined filtrates is ultimately precipitated with barium chloride, after the removal of residual silica, and the reduction of chromium, if present, with aluminum metal.

If barium is present and strontium and/or large amounts of calcium are absent, the acid-insoluble material obtained after sample decomposition is ignited, and fused with sodium carbonate to convert the insoluble barium sulphate (and lead sulphate, if present) to soluble sulphate. The melt is digested in water and the solution is filtered to remove barium carbonate. The sulphate in the resulting filtrate is precipitated, after the removal of residual silica, and the reduction of chromium and/or large amounts of iron, if present, with aluminum metal.

Refractory sulphide ores and other ores and mill products containing lead, barium, strontium, and/or calcium are decomposed by fusion with sodium carbonate and sodium peroxide to convert insoluble sulphates and other forms of sulphur to soluble sulphate. The melt is digested in water, and the resultant solution is ultimately filtered to remove the insoluble carbonates of the above elements, and the hydrous oxides of iron, manganese, copper, cobalt, nickel, titanium, zirconium, and magnesium. The sulphate in the resulting filtrate is precipitated after the removal of residual silica, and the reduction of chromium, if present, with aluminum metal.

Discussion of interferences

Lead, barium, strontium, and large amounts of calcium cause low results for sulphur if the acid-insoluble silica residue obtained by "wet" oxidation of elemental sulphur and sulphur compounds with bromine and nitric acid is neglected. These elements react with the sulphate produced to form insoluble sulphates that are retained in the acid-insoluble residue[1,2]. Sulphate in acid-insoluble residues containing lead, strontium or calcium sulphates is recovered by converting the insoluble sulphates to insoluble carbonates and soluble sulphate by treating a dilute ammoniacal ammonium nitrate solution of the sample, containing the residue, with ammonium carbonate[4]. By this procedure, any excess strontium and calcium, and also lead, which are present in the initial sample solution as soluble nitrates, and which would interfere in the subsequent precipitation of barium sulphate by forming insoluble sulphates, are also precipitated as insoluble carbonates and as the hydrous oxide by occlusion with hydrous ferric oxide, respectively, and subsequently separated from sulphate by filtration. Residues containing barium sulphate must be fused with sodium carbonate to convert the insoluble sulphate to soluble sulphate, followed by digestion of the melt in water, and filtration to remove the resultant insoluble barium carbonate[1,2]. Lead, strontium, and calcium sulphates are also converted to soluble sulphate by this procedure.

Large amounts of iron (III) cause low results for sulphur because of the co-precipitation of ferric sulphate with barium sulphate; ferric sulphate subsequently loses sulphur trioxide during ignition of the precipitate, and is converted to ferric oxide which weighs less than barium sulphate[1]. Small or moderate amounts of iron (III) do not cause appreciable error if barium sulphate is precipitated in an ammoniacal medium in the presence of hydrous ferric oxide, and the solution is subsequently acidified to dissolve the hydrous oxide. Interference from large amounts of iron (III), and from chromium (VI), which forms insoluble barium chromate, is avoided by reducing these elements (and lead, copper, and antimony, if present) to lower valence states with metallic aluminum[1-3]. Chromium (III) does not react with barium chloride, and co-precipitation of ferrous sulphate is minimized by precipitating the sulphate from a large volume of cold solution by the slow addition of barium chloride[1,3].

Large amounts of sodium, potassium, and ammonium salts cause low results for sulphur because they co-precipitate as sulphates and acid sulphates. This results in the substitution of a lighter element for barium in the weighed precipitate, and in the loss of sulphuric acid and ammonia during ignition. The co-precipitation of these compounds is minimized by precipitating the sulphate by the rapid addition of barium chloride to a hot solution[2,3].

Interference from nitric acid and nitrates, which are strongly occluded by the barium sulphate precipitate, is avoided by preliminary removal of these compounds by repeated evaporation of the sample solution to dryness with hydrochloric acid[1,2]. Positive error from molybdenum, which contaminates the precipitate[5], is eliminated by re-precipitating the sulphate after fusion of the ignited barium sulphate precipitate with sodium carbonate, digestion of the melt in water, separation of barium carbonate by filtration, and subsequent removal of the residual molybdenum from the filtrate by precipitation with alpha-benzoin oxime[6].

Silica, elements that form insoluble chlorides (e.g., silver, lead, and mercury), and elements that hydrolyze (e.g., titanium, zirconium, niobium, and tantalum) in the dilute hydrochloric acid medium employed for the precipitation of barium sulphate, are separated from sulphate either by filtration or by other separation procedures described under "Outline". Tungsten is not completely separated from sulphate by these procedures, but milligram-quantities may be present during the precipitation of sulphate without causing appreciable error in the sulphur result[7].

Range

The method is suitable for samples containing more than approximately 0.01% of sulphur.

Reagents

Bromine-carbon tetrachloride solution, 40% v/v. Mix 20 ml of bromine and 30 ml of carbon tetrachloride in a glass-stoppered bottle.

Bromine-potassium bromide solution, 10% v/v and 16% w/v, respectively. Dissolve 32 g of potassium bromide in a minimal volume of water, add 20 ml of bromine, mix, and dilute to 200 ml with water. Store in a glass-stoppered bottle.

Barium chloride solution, 10% w/v.

Silver nitrate solution, 1% w/v. Dissolve 1 g of silver nitrate in water, add 5-10 drops of concentrated nitric acid, and dilute to 100 ml with water.

Ferric nitrate solution, 15% w/v. Dissolve 15 g of ferric nitrate nonahydrate [$Fe(NO_3)_3.9H_2O$] in water and dilute to 100 ml.

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Ammonium carbonate solution, saturated.

Alpha-benzoin oxime solution, 5% w/v. Dissolve 5 g of the reagent in a solution containing 95 ml of acetone and 5 ml of water. Store in a dark-coloured bottle in a cool place. Prepare a fresh solution every five days.

Alpha-benzoin oxime wash solution, 0.025% w/v. Dilute 5 ml of the 5% solution to 1 litre with cold 1% hydrochloric acid. Prepare fresh as required.

Hydrochloric acid, 50% and 0.2% v/v.

Sodium carbonate wash solution, 1% w/v.

Aluminum powder (sulphur-free).

Procedures

In these procedures a reagent blank is carried along with the samples (Note 1).

A - Acid decomposition ("wet" oxidation) procedure for acid-soluble sulphide ores and mill products

(a) Lead, strontium, barium, chromium, and large amounts of calcium and iron absent

Transfer 0.2-1 g of sample (Note 2), ground to approximately 80 mesh (Note 3), and containing up to approximately 100 mg of sulphur, to a dry 400-ml beaker, and cover the beaker with a dry watch glass. Add 6-8 ml of 40% bromine-carbon tetrachloride solution (Notes 4 and 5), swirl the beaker to disperse the sample and, with occasional mixing, allow the mixture to stand at room temperature for 15 minutes. Add 10 ml of concentrated nitric acid and, with occasional mixing, allow the solution to stand for a further 15 minutes. Place the beaker in a hot water-bath, heat the solution at approximately 90°C until all action has ceased and most of the bromine has been expelled, then replace the cover with a ribbed watch glass and allow the solution to evaporate to dryness. Cool, wash down the sides of the beaker with 10-15 ml of concentrated hydrochloric acid, evaporate the solution to dryness in the water-bath again to remove nitric acid, and bake the residue in an oven for 1-2 hours at 100°C (Note 6) to dehydrate the silica.

Add 2 ml of concentrated hydrochloric acid and 50 ml of water to the residue, wash down the sides of the beaker and the watch glass with a small amount of water, and boil the solution for 5-10 minutes to ensure the complete dissolution of the soluble salts. Dilute to approximately 100 ml with water and heat the solution to the boiling point. Filter the solution (Whatman No. 40 paper) into a 600-ml beaker, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue.

Dilute the filtrate to approximately 400 ml with water (Note 7), and heat the solution to the boiling point.

Add several drops of 0.1% methyl red solution, neutralize the solution approximately with concentrated ammonium hydroxide to precipitate the hydrous oxide of iron, and add 5-10 drops in excess. While stirring, add 15 ml of 10% barium chloride solution, then add sufficient concentrated hydrochloric acid, by drops, to dissolve the iron precipitate, and add 2 ml in excess (Notes 8 and 9). Heat the solution to the boiling point, and allow the precipitate to settle for approximately 2 hours (Notes 10 and 11) or preferably overnight. Filter the resulting solution (Whatman No. 42 paper and paper pulp), transfer the precipitate quantitatively to the filter paper, and discard the filtrate. Place a clean beaker under the funnel, wash the paper and precipitate once or twice with cold 0.2% hydrochloric acid (Note 12), and then with hot water until the precipitate is free of chlorides (Notes 13 and 14).

Transfer the paper and precipitate to a tared 30-ml platinum crucible, dry and burn off the paper at as low a temperature as possible (Note 15), and ignite at 800-900°C.

If the sample does not contain molybdenum, cool the crucible in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained, and correct the result obtained for the sample by subtracting that obtained for the reagent blank.

If the sample contains molybdenum (Note 16), add 2-3 g of sodium carbonate to the ignited barium sulphate precipitate, and fuse the mixture at approximately 1100°C. Cool, transfer the crucible and contents to a 250-ml beaker and add 50 ml of water. Heat gently until the disintegration of the melt is complete, then remove the crucible after washing it thoroughly with hot water. Filter the resulting solution (Whatman No. 42 paper) into a 250-ml beaker, and wash the beaker, paper, and precipitate 12-15 times with warm water. Discard the paper and precipitate. Add several drops of 0.1% methyl red solution to the filtrate, neutralize the solution approximately with concentrated hydrochloric acid, and add 2 ml in excess. Cool the solution to 15-20°C, add some ashless paper pulp, and 2-3 ml (or more if necessary) of 5% alpha-benzoin oxime solution to precipitate the molybdenum present. Stir the solution thoroughly, filter it (Whatman No. 541 paper) into a 600-ml beaker, and wash the paper and precipitate 12-15 times with cold 0.025% alpha-benzoin oxime wash solution. Discard the paper and precipitate. Neutralize the solution approximately by adding concentrated ammonium hydroxide, by drops, then add 2 ml of concentrated hydrochloric acid, and dilute the solution to approximately 400 ml with water. Heat the solution to the boiling point and, while stirring, quickly add 15 ml of hot 10% barium chloride solution. Allow the precipitate to settle for 2 hours or overnight, then filter, wash (Note 17), ignite, and weigh the barium sulphate precipitate as described above.

(b) Lead, strontium, barium, and/or large amounts of calcium absent (chromium and/or large amounts of iron present)

Following sample decomposition, removal of nitric acid, and dehydration of silica as described above, add 4 ml of concentrated hydrochloric acid and 50 ml of water to the residue, wash down the sides of the beaker and the watch glass with a small amount of water, and boil the solution for 5-10 minutes to dissolve the soluble salts. Allow the solution to cool for 5 minutes, cover the beaker, and add 0.2 g of powdered aluminum metal. Mix, and heat gently until the solution becomes colourless or green, depending on the absence or presence of chromium, respectively. Wash down the sides of the beaker and the watch glass with water, filter the solution (Whatman No. 40 paper) into a 1-litre beaker, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue.

Dilute the filtrate to approximately 700 ml with water, and cool the solution to room temperature. By burette, and while stirring, add 25 ml of 10% barium chloride solution, by drops, at a rate not exceeding 2-3 ml per minute. Allow the precipitate to settle for approximately 2 hours or overnight, then proceed with the filtration, and subsequent treatment of the precipitate, including the removal of occluded molybdenum, if necessary, as described above.

(c) Lead, strontium, and/or large amounts of calcium present (barium absent)

Following sample decomposition, removal of bromine, and the initial evaporation of the solution to dryness as described in Procedure A (a), add 5 ml of concentrated nitric acid and approximately 50 ml of water to the residue, and boil the solution for 5-10 minutes to dissolve the soluble salts. Dilute the solution to approximately 150 ml with water and, if lead is present, add sufficient 15% ferric nitrate solution (Note 18), if necessary, so that the iron content of the solution is at least 20 times that of the lead. Heat the solution to the boiling point, add sufficient concentrated ammonium hydroxide to precipitate the hydrous oxide of iron, then add 1 ml in excess followed by 15 ml of saturated ammonium carbonate solution. Boil the solution for several minutes to coagulate the resulting mixed hydrous oxide and carbonate precipitate, filter it (Whatman No. 541 paper) into a 600-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hot water.

Using a jet of hot water, transfer the bulk of the precipitate to the original beaker, cover the beaker, and add sufficient concentrated nitric acid to dissolve the precipitate. Add 5 ml in excess and boil the solution for 5-10 minutes to expel carbon dioxide. Dilute to 150 ml with water and heat the solution to the boiling point. Re-precipitate the mixed hydrous oxides and carbonates (Note 19), filter the solution through the same filter paper, and wash the paper and precipitate as described above. Collect the filtrate and washings in the beaker containing the initial filtrate and discard the paper and precipitate.

Add several drops of 0.1% methyl red solution to the combined filtrates, and carefully neutralize the solution with concentrated hydrochloric acid. Add 10 ml in excess, and boil the solution for 5-10 minutes to expel carbon dioxide. Remove the cover, evaporate the solution to approximately 30 ml, then add 10 ml of concentrated hydrochloric acid, cover the beaker, and boil the solution for about 30 minutes to destroy ammonium salts. Replace the cover with a ribbed watch glass, place the beaker in a hot water-bath, and allow the solution to evaporate to dryness. Cool, wash down the sides of the beaker with 10-15 ml of concentrated hydrochloric acid, and evaporate the solution to dryness in the water-bath again. Repeat the hydrochloric acid treatment and evaporation two more times to ensure the complete removal of ammonium nitrate, and bake the residue as described in Procedure A (a). Add 2 ml of concentrated hydrochloric acid and 50 ml of water to the residue, wash down the sides of the beaker and the watch glass with a small amount of water, and boil the solution for 5-10 minutes to dissolve the salts.

If chromium is absent, filter the solution (Whatman No. 40 paper), if necessary, into a 600-ml beaker to remove residual silica, and dilute the filtrate to 400 ml with water. Heat the solution to the boiling point and, while stirring, precipitate barium sulphate by the slow addition, by drops, of 15 ml of 10% barium chloride solution. Allow the precipitate to settle, then proceed with the filtration and subsequent treatment of the precipitate (Note 17) as described in Procedure A (a).

If chromium is present, add 2 ml of concentrated hydrochloric acid, heat the solution to the boiling point, and proceed with the reduction of chromium, the precipitation of barium sulphate, and the subsequent determination of sulphur as described in Procedure A (b).

(d) Barium present (strontium and/or large amounts of calcium absent

Following sample decomposition, dissolution of the residue in dilute hydrochloric acid, and filtration of the resulting solution to remove acid-insoluble material as described in Procedure A (a), transfer the paper and residue to a 30-ml platinum or porcelain crucible (Note 20), burn off the paper at a low temperature, and ignite at 600-700°C. Fuse the residue with 1-2 g of sodium carbonate, cool, and transfer the crucible and contents to a 250-ml beaker. Add approximately 75 ml of water, heat gently until the disintegration of the melt is complete, then remove the crucible after washing it thoroughly with hot water. Filter the resulting solution (Whatman No. 42 paper) into a 250-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hot 1% sodium carbonate solution. Discard the paper and precipitate.

Add several drops of 0.1% methyl red solution to the filtrate, and carefully neutralize the solution with concentrated hydrochloric acid. Add 5 ml in excess, and boil the solution for 5-10 minutes to expel carbon dioxide. Evaporate the solution to approximately 25 ml, then evaporate it to dryness in a hot water-bath, and bake the residue as described in Procedure A (a) to dehydrate residual silica. Add 25 ml of water and 5-10 drops of concentrated hydrochloric acid to the residue, and boil for 5 minutes to dissolve the soluble salts. Filter the solution (Whatman No. 40 paper) into the beaker containing the initial filtrate, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue.

If chromium and/or large amounts of iron are absent, dilute the solution to approximately 400 ml with water, and proceed with the precipitation of barium sulphate and the subsequent determination of sulphur as described in Procedure A (a).

If chromium and/or large amounts of iron are present, add 2 ml of concentrated hydrochloric acid, evaporate the solution to approximately 50 ml, and proceed with the reduction of chromium and iron, the precipitation of barium sulphate, and the subsequent determination of sulphur as described in Procedure A (b).

B - <u>Fusion procedure for refractory sulphide and other ores and mill products (lead, barium, strontium, and/or calcium present)</u>

Transfer 0.2-2 g of sample, containing up to approximately 100 mg of sulphur, to a 60-ml iron crucible, and add 1 g of sodium carbonate and a six-fold weight excess of sodium peroxide. Mix thoroughly, and place the crucible in a hole in a piece of asbestos board (Note 21). Cover the crucible, heat the mixture over an open flame at a temperature just sufficient to produce fusion, and maintain it in the molten state for several minutes to ensure complete sample decomposition. Remove the cover and swirl the crucible to distribute the melt in a thin layer around the inner walls. Allow the melt to cool, then transfer the crucible and cover to a 400-ml (covered) beaker containing approximately 100 ml of water. When the subsequent reaction has ceased, remove the crucible and cover after washing them thoroughly with hot water, and boil the solution for at least 10 minutes to destroy the residual peroxide. Add 1-2 ml of ethyl alcohol to reduce manganate or permanganate ion, if present, and boil the solution for a further 5 minutes to precipitate manganese as the dioxide. Using a Buchner funnel and suction, filter the resulting solution (Whatman No. 52 paper), and wash the paper and precipitate at least 10 times with hot 1% sodium carbonate solution. Discard the paper and precipitate.

Transfer the filtrate to a 600-ml beaker, add several drops of 0.1% methyl red solution, and carefully neutralize the solution with concentrated hydrochloric acid. Add 10 ml in excess, and boil the solution for 5-10 minutes to expel carbon dioxide. Evaporate the solution to approximately 30 ml, then place the beaker in a hot water-bath, evaporate the solution to dryness, and bake the residue as described in Procedure A (a) to dehydrate the residual silica. Add 2 ml of concentrated hydrochloric acid and 50 ml of water to the residue, and wash down the sides of the beaker with a small amount of water. Boil the solution for 5-10 minutes to dissolve the salts then, depending on the absence or presence of chromium, proceed with the precipitation of barium sulphate and the subsequent determination of sulphur as described in Procedure A (c).

<u>Notes</u>

1. In exact work, a reagent blank should be carried along with the samples because of the presence of oxides of sulphur in the laboratory air and in the reagents employed.

2. Only acid-soluble sulphate and sulphide are obtained by treatment of the sample with acids in an oxidizing environment. If the presence of acid-insoluble sulphide minerals is suspected, the sample should be decomposed by fusion with sodium carbonate and sodium peroxide as described in Procedure B. Neither Procedures A (a) to (d) nor B are applicable to samples containing large amounts of tungsten.

3. To avoid oxidation of sulphide minerals, samples containing sulphides, particularly pyrite, should not be ground finer than approximately 100 mesh. Fine grinding causes slight losses of sulphur as the dioxide and appreciable formation of sulphate[2].

4. The oxidation of the sample with bromine and nitric acid should be carried out in a well-ventilated fume hood.

5. The addition of 10 ml of 10% bromine-16% potassium bromide solution, rather than the 40% bromine-carbon tetrachloride solution, is recommended for pyrrhotite ores. If the more concentrated bromine-carbon tetrachloride solution is added to samples of these ores, loss of sulphur may occur because of the violence of the resulting reaction[1].

6. Care must be taken to avoid overheating the residue or else sulphur may be lost by volatilization as the trioxide.

7. The volume of the solution in which sulphate is to be precipitated should be relatively large to minimize the adsorption of other ions by the resultant barium sulphate.

8. The final solution should contain only a small excess of hydrochloric acid (i.e., a concentration of approximately 0.05 M) because the solubility of barium sulphate increases with increasing acid concentration. In the presence of an excess of barium chloride the solubility of the precipitate is very small at this acid concentration. The presence of a small excess of hydrochloric acid is necessary to prevent the co-precipitation of the hydrous oxide of barium; to promote the formation of a coarse, easily-filterable precipitate; and to prevent the possible precipitation of barium compounds such as the carbonate and phosphate, which are insoluble in neutral or basic solutions[3].

9. If the sample contains an appreciable amount of manganese, any manganese dioxide that has not re-dissolved at this stage may be dissolved by the addition of several drops of 30% hydrogen peroxide.

10. The co-precipitation or occlusion of other ions is reduced by digesting the precipitate in hot solution, and/or allowing it to stand for several hours before filtration[1-3].

11. The completeness of precipitation can be tested, prior to filtration, by adding several drops of barium chloride solution to the supernatant liquid.

12. The dilute hydrochloric acid wash facilitates the removal of ferric iron from the paper and precipitate.

13. The complete removal of chloride ion is indicated when the addition of several drops of 1% silver nitrate solution to a small portion of the last washings yields a clear solution (i.e., absence of silver chloride) or only a very faint opalescence.

14. Except in the most exact work, the small loss of barium sulphate resulting from its solubility in the wash water may be neglected. In exact work, this residual barium sulphate may be recovered as follows:

Evaporate the washings to dryness, dissolve the residue in 1 ml of 50% hydrochloric acid, and add 25 ml of hot water. Add 2 ml of 10% barium chloride solution, and digest the solution at 70-80°C for several hours. Filter the solution, transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate with hot water. Proceed as described with the ignition and weighing of the precipitate, and add the result obtained to that obtained for the main precipitate.

15. Because barium sulphate is easily reduced by carbon, the filter paper should not be allowed to burst into flame during the burning or charring process, which should be carried out at temperatures below 600°C under oxidizing conditions. When the paper has been completely charred, the carbon may be burned off by raising the temperature until the crucible is dull red[2]. A more convenient way to accomplish drying, charring, and ignition of the paper and precipitate is to place the crucible and contents in a cold muffle furnace. When the heat is turned on, the drying, charring, and ignition usually proceed satisfactorily without further attention. Reduction and mechanical loss of barium sulphate can also be avoided by collecting the precipitate in a Gooch crucible. The crucible should be dried at 100-120°C before ignition of the precipitate at 800-900°C.

16. The presence of occluded molybdenum is indicated by the yellowish-green colour of the ignited precipitate.

17. Because barium sulphate is precipitated in the absence of iron at this stage, the dilute hydrochloric acid wash may be omitted.

18. One ml of 15% ferric nitrate nonahydrate solution contains approximately 21 mg of iron (III).

19. Because sulphate is strongly occluded by hydrous ferric oxide in weakly ammoniacal media, re-precipitation of the mixed hydrous oxides and carbonates is necessary to recover the occluded sulphate[1].

20. If the residue contains lead sulphate and lead chloride, a porcelain crucible should be employed for ignition. If a platinum crucible is used, lead compounds may be reduced to the metallic state by the carbon from the filter paper, or by reducing gases from the flame, and will subsequently alloy with, and contaminate the crucible.

21. When a flame is employed for fusion of the sample, an asbestos shield is required to prevent contamination of the melt by sulphur contained in the gas employed for the flame. This contamination can be avoided by using a muffle furnace for sample fusion.

Calculations

$$\% \text{ S} = \frac{0.1374 \times (W_P - W_B)}{\text{Sample weight (g)}} \times 100$$

where:

W_P = weight (g) of the ignited barium sulphate precipitate.

W_B = weight (g) of the ignited blank.

Other applications

The methods described in Procedures A (a) to (d) can be employed to determine sulphur in sulphide minerals. The method described in Procedure B is applicable to silicate rocks and minerals[1,2].

References

1. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 1003-1011, 1037 (1962).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 711-722 (1953).

3. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 329-343 (1948).

4. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, 503, 516 (1939).

5. D.A. Lambie and W.R. Schoeller, Analyst, <u>65</u>, 281 (1940).

6. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E31-67, pp 107-108 (1971).

7. Idem, ibid., Part 32, E352-70, pp 893-894 (1971).

DETERMINATION OF TANTALUM IN TANTALUM AND NIOBIUM ORES AND MILL PRODUCTS BY PRECIPITATION WITH AMMONIUM HYDROXIDE AFTER SEPARATION BY SOLVENT EXTRACTION

Principle

This method is based on that developed by Faye and Inman[1], and involves the separation of tantalum from certain matrix elements by methyl isobutyl ketone extraction of its fluoride complex from a 0.75 M hydrofluoric-1 M nitric acid medium. Tantalum is stripped from the ketone phase with dilute hydrogen peroxide, and determined by weighing as the oxide after precipitation as the hydrous oxide with ammonium hydroxide.

Outline

The sample is decomposed with hydrofluoric and nitric acids, and the solution is ultimately centrifuged to remove acid-insoluble material. Tantalum is separated from niobium and other matrix elements by a three-stage methyl isobutyl ketone extraction of its fluoride complex, and then stripped from the combined extracts by shaking with dilute hydrogen peroxide. After re-extraction of the tantalum to remove co-extracted elements, hydrogen peroxide and co-extracted hydrofluoric acid are removed from the resultant aqueous phase by evaporation with sulphuric acid. The tantalum in the resulting solution is ultimately precipitated with ammonium hydroxide, and the precipitate is separated by filtration, ignited, and weighed.

Discussion of interferences

The extraction procedure eliminates interference from niobium, and from other elements that are completely (e.g., iron, aluminum, titanium, lead, zirconium, hafnium, tin, and uranium) or partly (e.g., magnesium, calcium, and manganese) precipitated as the hydrous oxides from an ammonium hydroxide medium[1-4].

Cerium and thorium, which form insoluble fluorides, and tungsten, which is partly precipitated as an insoluble compound during the decomposition of the sample[3], are separated from tantalum by centrifugation, before the extraction of the fluotantalate complex. Interference from molybdenum and residual tungsten, which may co-extract to some extent with the tantalum, is avoided by precipitating the hydrous oxide of tantalum in the presence of an excess of ammonium hydroxide.

Range

The method is suitable for samples containing more than approximately 0.5% of tantalum.

Apparatus

Polypropylene separatory funnels. 250- and 500-ml pear-shape type.

Polypropylene centrifuge tubes. 50-ml.

Reagents

Hydrofluoric-nitric acid solution, 0.75 M and 1 M, respectively. Add 27 ml of concentrated hydrofluoric acid and 64 ml of concentrated nitric acid to a 1-litre polyethylene bottle, and dilute to 1000 ml with water.

Hydrogen peroxide, 1.5% w/v. Dilute 50 ml of 30% hydrogen peroxide to 1 litre with water.

Methyl isobutyl ketone, equilibrated. Transfer approximately 300 ml of analytical reagent-grade solvent and 100 ml of 0.75 M hydrofluoric-1 M nitric acid solution to a 500-ml polypropylene separatory funnel, stopper, and shake for 2 minutes. Allow several minutes for the layers to settle, then drain off and discard the lower aqueous layer. Store the resulting methyl isobutyl ketone in a polyethylene bottle (Notes 1 and 2).

Methyl red indicator solution, 0.1% w/v in ethyl alcohol. Store in a dropping bottle.

Ammonium hydroxide wash solution, 1% v/v.

Sulphuric acid, 50% v/v.

Procedure

Transfer 0.2-2 g of sample, ground to at least minus 200 mesh (Note 3), and containing up to approximately 100 mg of tantalum, to a 100-ml platinum dish (Note 4), and add 20 ml of concentrated hydrofluoric acid and 10 ml of concentrated nitric acid. Swirl the dish to disperse the sample, cover it with a Teflon cover, and heat gently until the decomposition of acid-soluble material is complete (Note 5). Remove the cover and, carefully, without baking, evaporate the solution to near dryness or until the fluoride salts have crystallized. Add exactly 0.6 ml of concentrated hydrofluoric acid (plastic pipette) (Note 6) and 1.5 ml of concentrated nitric acid to the residue, by drops, heat gently (Note 7) to dissolve the crystallized fluorides, and add exactly 23 ml of water. Stir the resulting suspension thoroughly with a platinum or plastic rod, and pour the mixture into a 50-ml polypropylene centrifuge tube. Centrifuge the mixture for 1-2 minutes, then pour the supernatant solution into a dry 250-ml polypropylene separatory funnel. Wash the platinum dish with 8 ml of 0.75 M hydrofluoric-1 M nitric acid solution, and pour the solution into the centrifuge tube containing the acid-insoluble residue. Stir the wash solution and residue thoroughly, centrifuge for 1 minute, and pour the supernatant solution into the separatory funnel containing the initial sample solution. Wash the platinum dish two more times with 8-ml portions of the hydrofluoric-nitric acid solution, and add the washings to the initial solution.

Add 25 ml of equilibrated methyl isobutyl ketone to the solution in the separatory funnel, stopper tightly, and shake for 1 minute. Allow several minutes for the layers to separate, then drain the lower aqueous phase into a second 250-ml separatory funnel, and drain the methyl isobutyl ketone phase into a third separatory funnel. Add 25 ml of the equilibrated ketone to the second funnel containing the aqueous phase, stopper, and shake for 1 minute. After the layers have separated, drain the lower aqueous phase into the first funnel, and drain the ketone phase into the third funnel containing the initial ketone extract. Wash the second funnel, by shaking for 30 seconds each time, with two 5-ml portions of methyl isobutyl ketone. Add the washings and an additional 15 ml of the ketone to the first funnel, and re-extract the solution by shaking for 1 minute. Drain off and discard the aqueous phase. Drain the ketone phase into the third funnel, wash the first funnel with two 5-ml portions of the ketone as described above, and add the washings to the combined extracts.

Add 25 ml of 1.5% hydrogen peroxide to the combined extracts, stopper, and shake for 1 minute. Allow the layers to separate, then drain the lower aqueous layer into a large (approximately 175 ml capacity) platinum dish. Strip the combined extracts three more times, by shaking for 1 minute each time, with 25-ml portions of 1.5% hydrogen peroxide (Note 8), and combine the aqueous layers with the first layer. Cover the combined solution with a Teflon cover, heat gently until the decomposition of hydrogen peroxide is complete, then remove the cover and evaporate the solution to near dryness or until the salts have crystallized.

Add 0.6 ml of concentrated hydrofluoric acid and 1.5 ml of concentrated nitric acid to the residue, warm gently to dissolve the crystallized fluorides, and add 23 ml of water. Transfer the solution to a 250-ml polypropylene separatory funnel, and wash the dish with three 8-ml portions of 0.75 M hydrofluoric-1 M nitric acid solution. Add the washings to the funnel, then re-extract the solution with equilibrated methyl isobutyl ketone, and strip the tantalum from the combined extracts again with 1.5% hydrogen peroxide as described above.

Add 8 ml of 50% sulphuric acid to the combined hydrogen peroxide solutions, cover the solution with a Teflon cover, and heat gently until the decomposition of hydrogen peroxide is complete. Remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the dish with water, and evaporate the solution to fumes again to ensure the complete removal of co-extracted hydrofluoric acid (Notes 9 and 10). Cool, add 25 ml of water and several drops of 0.1% methyl red solution, and neutralize the solution approximately with concentrated ammonium hydroxide. Add 5 ml in excess, and heat the solution gently to coagulate the resulting tantalum hydrous oxide precipitate. Filter the solution (Whatman No. 541 paper), transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate thoroughly with hot 1% ammonium hydroxide.

Transfer the paper and precipitate to a tared 30-ml platinum crucible, burn off the paper at a low temperature, ignite at approximately 1000°C, cool in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained.

Notes

1. Methyl isobutyl ketone extracts an appreciable amount of hydrofluoric acid and other mineral acids from aqueous media. Consequently, pre-equilibration of the ketone, by shaking with a hydrofluoric-nitric acid solution of the same concentration as that subsequently employed as the extraction medium for the separation of tantalum, is necessary to minimize the co-extraction of these acids from the sample solution during the extraction of tantalum[1,3].

2. The interface between the ketone and the aqueous phase can be clearly seen against a bright diffused light.

3. Complete decomposition of tantalum-bearing minerals may not be obtained by the described procedure if the sample is in a coarser state[5].

4. Teflon beakers can be used for sample decomposition rather than platinum dishes. However, these beakers are not recommended for the subsequent precipitation of tantalum as the hydrous oxide because of the visual difficulty involved in transferring the white precipitate quantitatively from the white, rough-textured beaker to the filter paper.

5. Repeated treatment of the sample with hydrofluoric acid may be necessary for complete decomposition of certain tantalum minerals (e.g., tantalite)[6].

6. Because hydrofluoric acid volatizes from aqueous solutions on prolonged standing at room temperature, it should not be added to the residue unless the subsequent extraction of tantalum is to be performed without appreciable delay.

7. The platinum dish and contents should not be heated to temperatures above approximately 70°C or else an appreciable amount of hydrofluoric acid will be lost by volatilization.

8. The methyl isobutyl ketone remaining in the separatory funnel can be used again, after washing with water and pre-equilibration with 0.75 M hydrofluoric-1M nitric acid solution.

9. Partial hydrolysis of tantalum may occur during the evaporation of the solution to fumes of sulphur trioxide, but this does not affect the subsequent determination of tantalum.

10. If the sample solution has inadvertently been evaporated to dryness, add 1-2 ml of concentrated hydrofluoric acid and 8 ml of 50% sulphuric acid, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the dish with a small amount of water, evaporate to fumes again to ensure the complete removal of hydrofluoric acid, then proceed as described.

Calculations

$$\% \ Ta_2O_5 = \frac{\text{Weight of ignited precipitate (g)}}{\text{Sample weight (g)}} \times 100$$

$$\% \ Ta = 0.8190 \times \% \ Ta_2O_5$$

References

1. G.H. Faye and W.R. Inman, Trans. Can. Inst. Mining Met., 60, 343 (1957).

2. P.C. Stevenson and H.G. Hicks, Anal. Chem., 25, 1517 (1953).

3. G.W.C. Milner, G.A. Barnett and A.A. Smales, Analyst, 80, 380 (1955).

4. G.R. Waterbury and C.E. Bricker, Anal. Chem., 29, 1474 (1957).

5. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 6, pp 222-223 (1964).

DETERMINATION OF ZIRCONIUM IN ORES AND MILL PRODUCTS BY PRECIPITATION WITH MANDELIC ACID

Principle

This method[1] is based on that developed by Kumins[2], and involves the precipitation of zirconium as the tetramandelate from a hydrochloric acid medium. Zirconium is determined by weighing as the oxide after ignition of the precipitate.

Outline

The sample is decomposed by fusion with sodium peroxide, and the melt is digested in water. The hydrous oxide of zirconium is separated from sulphate, phosphate, and from some silica, niobium, and tantalum by filtration, and the precipitate is dissolved in hydrochloric acid. The residual zirconium retained in the filter paper as the hydrous oxide or phosphate is ultimately recovered as the hydrous oxide, and the precipitate is ignited and fused with potassium pyrosulphate. The melt is dissolved in dilute hydrochloric acid, and the solution is combined with the initial solution. The zirconium in the resulting solution is precipitated with mandelic acid, and the precipitate is separated by filtration and ignited. After fusion of the residue with potassium pyrosulphate and dissolution of the melt,zirconium is re-precipitated to remove occluded iron and silica, and the precipitate is ignited and weighed.

If large amounts of silica, phosphate, niobium, and/or tantalum are present in the sample, these occluded impurities are separated from zirconium by repeated fusion of the initial ignited precipitate with potassium carbonate, followed by digestion of the melt in water, and separation of the hydrous oxide of zirconium by filtration. After dissolution of the precipitate and recovery of the residual zirconium in the filter paper, zirconium is ultimately re-precipitated with mandelic acid.

Discussion of interferences

Sulphate and phosphate interfere in the determination of zirconium by complexing it and inhibiting its precipitation as the tetramandelate, and by forming insoluble zirconium phosphate, respectively. Silica, niobium, and tantalum interfere because of the coprecipitation of their hydrous oxides with the zirconium tetramandelate precipitate[1,3]. Zirconium is separated from moderate amounts of sulphate and phosphate, from some silica, niobium, and tantalum, and from molybdenum, tungsten, chromium, tin, arsenic, lead, uranium, vanadium, aluminum, and zinc by the sodium peroxide separation procedure.

Positive error from small amounts of iron and silica, which contaminate the initial zirconium tetramandelate precipitate, is eliminated by re-precipitating the zirconium, after fusion of the initial zirconium dioxide residue with potassium pyrosulphate. Positive error from occluded silica, phosphate, niobium and/or tantalum can be avoided by removing these elements from the initial zirconium dioxide residue, before re-precipitation of zirconium tetramandelate, by repeated fusions of the residue with potassium carbonate, followed by digestion of the melt in water and filtration of the resultant hydrous zirconium oxide[1].

Hafnium interferes in this method because it also forms a precipitate with mandelic acid under the conditions employed for the precipitation of zirconium[1,2].

Range

The method is suitable for samples containing more than approximately 0.1% of zirconium.

Reagents

Mandelic acid solution, 16% w/v.

Mandelic acid wash solution, 5% w/v. Dissolve 50 g of the reagent in water, add 20 ml of concentrated hydrochloric acid, and dilute to 1 litre with water.

Ammonium chloride-ammonium hydroxide wash solution, 2% w/v and 1% v/v, respectively.

Hydrogen peroxide wash solution, 6% w/v. Dilute 20 ml of 30% hydrogen peroxide to 100 ml with water.

Potassium carbonate wash solution, 2% w/v.

Hydrochloric acid, 50% and 20% v/v.

Procedures

Large amounts of silica, phosphate, niobium, and/or tantalum absent

Transfer 0.2-2 g of powdered sample, containing up to approximately 100 mg of zirconium, to a 60-ml iron crucible, add approximately a five-fold weight excess of sodium peroxide and mix thoroughly. Cover the crucible, fuse the mixture over a low flame, and maintain it in the molten state for several minutes to ensure complete sample decomposition. Allow the melt to cool, then transfer the crucible and cover to a 600-ml (covered) beaker containing approximately 200 ml of water. When the subsequent reaction has ceased, remove the crucible and cover after washing them thoroughly with water, and allow the solution to digest on a hot-plate for 30 minutes to ensure the complete precipitation of the hydrous oxides of zirconium and iron. Using a Buchner funnel and suction, filter the resulting solution (Whatman No. 40 or 52 paper) (Note 1), transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate thoroughly with 2% ammonium chloride-1% ammonium hydroxide solution (Note 2). Discard the filtrate. Dissolve the precipitate, using five 10-ml portions of 50% hydrochloric acid, wash the paper with 10-15 ml of cold 6% hydrogen peroxide, and collect the resulting solution in a 400-ml beaker.

Transfer the filter paper (Note 3) to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 600°C. Cool and fuse the residue with a small amount of sodium carbonate. Cool, transfer the crucible and contents to a 250-ml beaker, and add approximately 50 ml of water. Heat gently until the disintegration of the melt is complete, then remove the crucible after washing it thoroughly with hot water. Filter the resulting solution (Whatman No. 40 paper), transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate thoroughly with hot water. Discard the filtrate.

Re-ignite the paper and precipitate as described above, and fuse the residue with a small amount of potassium pyrosulphate (Note 4). Cool, add 10 ml of 50% hydrochloric acid to the melt, heat gently until dissolution is complete, filter, if necessary, and add the filtrate to the initial solution contained in the 400-ml beaker.

Dilute the resulting solution to 150 ml with water and add 50 ml of 16% mandelic acid solution. Slowly heat the solution to approximately 85°C, and digest the resultant zirconium tetramandelate precipitate at this temperature for 1-2 hours. Allow the solution to stand at room temperature for several hours, or overnight if the amount of precipitate is small, then filter the solution (Whatman No. 42 paper) (Note 5), and wash the paper and precipitate 8-10 times with hot 5% mandelic acid solution.

Transfer the paper and precipitate to a platinum crucible, burn off the paper at a low temperature, and ignite at approximately 750°C. Fuse the resulting zirconium dioxide residue (Note 6) with 1-2 g of potassium pyrosulphate (Note 3), and transfer the crucible and contents to a 250-ml beaker. Add 75 ml of 20% hydrochloric acid and heat gently to dissolve the melt. Remove the crucible after washing it thoroughly with 20% hydrochloric acid and, if silica is present, filter the solution (Whatman No. 40 paper) into the beaker in which the precipitation was carried out. Wash the beaker, paper, and residue thoroughly with 20% hydrochloric acid, and discard the paper and residue. Dilute the resulting solution to 150 ml with 20% hydrochloric acid and re-precipitate the zirconium mandelate. Filter the solution, transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate as described above.

Transfer the paper and precipitate to a tared platinum crucible, ignite for 1 hour at 900-1000°C, cool in a dessicator and weigh. Repeat the ignition and weighing until constant weight is obtained.

Large amounts of silica, phosphate, niobium, and/or tantalum present

Following the initial precipitation and ignition of the zirconium tetramandelate precipitate as described above, fuse the resultant zirconium dioxide residue with 1-2 g of potassium carbonate. Cool, transfer the crucible and contents to a 250-ml beaker, and add approximately 50 ml of water. Heat gently until the disintegration of the melt is complete, then remove the crucible after washing it thoroughly with water. Add a small amount of paper pulp to the resulting solution, filter the solution (Whatman No. 40 paper) (Note 5), and wash the beaker, paper, and precipitate thoroughly with 2% potassium carbonate solution and hot water. Discard the filtrate.

Transfer the paper and precipitate to a platinum crucible, burn off the paper at a low temperature, and ignite at 750°C. Repeat the fusion and subsequent filtration once for samples with high silica, phosphate, and/or niobium contents, or twice for those with high tantalum contents, using the same beaker for the disintegration of the potassium carbonate melts. Dissolve the resultant precipitate, using 30 ml of 50% hydrochloric acid, wash the paper thoroughly with hot water, and collect the solution in the beaker that originally contained the zirconium tetramandelate precipitate. Wash the beaker that was employed for the disintegration of the potassium carbonate melts with approximately 20 ml of 50% hydrochloric acid followed by hot water, and add the washings to the main solution containing the zirconium. Ignite the filter paper at 600°C in a platinum crucible, and fuse any resulting residue with a small amount of potassium pyrosulphate. Cool, dissolve the melt in 10 ml of 50% hydrochloric acid and, if necessary (Note 7), filter the solution. Add the filtrate to the main solution then proceed with the re-precipitation of zirconium tetramandelate, and the subsequent treatment of the precipitate as described above.

Notes

1. Re-filter the solution if the filtrate is turbid.

2. Co-precipitated hydrous oxides (i.e., copper, nickel, calcium, and magnesium) are removed by washing the precipitate with ammoniacal ammonium chloride solution.

3. Because of the insolubility of zirconium phosphate in acid media, and the possible hydrolysis of zirconium during the dissolution of the hydrous oxide precipitate, some zirconium is usually retained on the filter paper. This must be recovered and added to the main solution.

4. Although large amounts of sulphate inhibit the precipitation of zirconium tetramandelate[2,4], 1-2 g of potassium pyrosulphate can be employed for fusion of the residue if 1-2 hours are allowed for the digestion of the subsequent precipitate.

5. It is not necessary to transfer the precipitate quantitatively to the filter paper at this stage, but the amount that remains in the beaker should be as small as possible.

6. Instead of igniting the zirconium tetramandelate precipitate and fusing the resulting impure oxide residue, Hill and Miles[4] re-precipitate the zirconium after dissolution of the initial precipitate in 20% ammonium hydroxide, followed by filtration of the ammoniacal solution to remove silica and compounds that are initially co-precipitated because of hydrolysis. This method is more rapid, and may possibly be better than the method described, particularly if the sample contains niobium and/or tantalum.

7. If some siliceous residue still remains at this stage, ignite the filter paper in a platinum crucible, cool, and add 5 ml of 50% sulphuric acid and 2 ml of concentrated hydrofluoric acid. Evaporate the solution until most of the sulphuric acid has

been expelled, and add approximately 3 ml of concentrated hydrochloric acid. Heat gently to dissolve the salts, filter the solution, add the filtrate to the main solution, then proceed as described.

Calculations

% ZrO_2

$$= \frac{\text{Weight of ignited precipitate (g)}}{\text{Sample weight (g)}} \times 100$$

Other applications

With modifications in the decomposition and separation procedures, this method can be employed to determine zirconium in minerals, zirconium metal and alloys, steel and ferrous alloys, magnesium alloys, and other nonferrous alloys[5].

References

1. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Mines Branch Monograph 866, Method No. Zr-1, Part III, April (1958).

2. C.A. Kumins, Anal. Chem., 19, 376 (1947).

3. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 5, pp 95-97 (1961).

4. J.H. Hill and M.J. Miles, Anal. Chem., 31, 252 (1959).

5. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 5, pp 120-125 (1961).

PART V

VOLUMETRIC METHODS

DETERMINATION OF ANTIMONY IN ORES AND MILL PRODUCTS BY TITRATION WITH POTASSIUM BROMATE AFTER REDUCTION WITH SODIUM SULPHITE

Principle

This method[1,2] involves the reduction of antimony to the trivalent state with sodium sulphite in an approximately 6 M sulphuric acid medium after separation as the trisulphide. Antimony is determined by titration of the resultant antimony (III) with potassium bromate in an approximately 2 M sulphuric-hydrochloric acid medium, in the presence of Bordeaux as internal indicator.

The corresponding reactions for these processes are:

$$Sb^{+5} + 2H^+ + SO_3^{=} \rightarrow Sb^{+3} + H_2O + SO_2\uparrow$$

$$BrO_3^- + 3Sb^{+3} + 6H^+ \rightarrow Br^- + 3Sb^{+5} + 3H_2O.$$

Outline

The sample is decomposed by heating with potassium pyrosulphate and sulphuric acid, in the presence of tartaric acid, which reduces antimony and arsenic to the trivalent state. The melt is dissolved in tartaric acid solution and acid-insoluble material is removed by filtration. The residual antimony in the residue is ultimately recovered as the sulphide. After dissolution of the sulphide precipitate, and removal of elemental sulphur by evaporation with sulphuric acid, the resultant solution is added to the initial filtrate, and arsenic is precipitated as the trisulphide from a strong hydrochloric acid medium and separated from antimony by filtration. Antimony, copper, and other elements of the copper and arsenic groups that may be present in the filtrate (lead, cadmium, bismuth, tin, palladium, gold, selenium, tellurium, molybdenum, and mercury) are subsequently precipitated as the sulphides from a dilute hydrochloric acid medium and separated from iron, vanadium, aluminum, cobalt, nickel, manganese, zinc, thallium, alkaline earths, and rare earths by filtration. The mixed sulphide precipitate is digested in potassium sulphide-potassium hydroxide solution, and the solution is filtered to remove the insoluble sulphides of copper, lead, cadmium, bismuth, palladium, and mercury. The antimony in the filtrate is ultimately reduced with sodium sulphite and titrated with potassium bromate solution.

Alternatively, following sample decomposition by treatment with potassium pyrosulphate and sulphuric acid, or by fusion with potassium carbonate and potassium nitrate, and the separation of arsenic by distillation as the trichloride as described in the Volumetric-Distillation-Bromate Method for arsenic (Procedures A and B, pp 236 and 237, Note 13) antimony can be determined as follows:

> Tartaric acid is added to the solution remaining in the distillation flask, and the residual antimony in the acid-insoluble material, obtained either before or after the distillation step, is ultimately recovered as the sulphide and treated as described above. Antimony is ultimately determined as described above, after its separation as the sulphide and digestion of the mixed sulphide precipitate in potassium sulphide-potassium hydroxide solution to remove the insoluble sulphides of the interfering elements.

Discussion of interferences

Arsenic, iron, copper, vanadium, and thallium interfere in the determination of antimony because they are also reduced to lower oxidation states with sodium sulphite in sulphuric acid media, and are subsequently oxidized by the potassium bromate[1-4]. Copper also interferes because the cuprous ion that is formed during reduction with sodium sulphite is partly air-oxidized to the divalent state prior to the titration of the antimony; this causes error in the antimony result because of the catalytic co-oxidation of antimony (III) to the pentavalent state with the copper (II)[1,5,6]. Large amounts of calcium and magnesium salts cause high results for antimony[1,2].

Lead sulphate, in large amounts, causes low results because antimony is partly retained by this compound[2]. Antimony is recovered from residues containing lead sulphate by fusing the residue with potassium carbonate and sulphur, followed by digestion of the melt in water, and filtration to remove lead carbonate and/or lead sulphide[2].

Interference from arsenic is eliminated by separating it from antimony either by precipitation as the trisulphide, or by distillation as the trichloride from an approximately 8 M hydrochloric acid medium[1,2]. Interference from iron, vanadium, thallium, calcium, and magnesium is avoided by separating antimony from these elements by precipitation as the sulphide from an approximately 1.6 M hydrochloric acid medium[1,2,7]. Antimony is separated from co-precipitated copper and lead sulphides, which are insoluble in alkaline sulphide media, by digestion of the mixed sulphide precipitate in potassium sulphide-potassium hydroxide solution[8].

Zinc, silver, tin, chromium, and moderate amounts of lead do not interfere in this method[1,2,5,6]. Selenium, tellurium, and gold may interfere.

Range

The method is suitable for samples containing more than approximately 0.01% of antimony.

Reagents

Standard potassium bromate solution, 0.05 N. Dissolve 2.7835 g of the reagent (dried at 180°C for 1-2 hours) in water, and dilute to 2 litres (Note 1).

Standard potassium bromate solution, 0.01 N. Dilute 100 ml of the 0.05 N solution to 500 ml with water.

Bordeaux indicator solution, 0.1% w/v. Store in a dropping bottle.

Potassium bromide solution, 10% w/v.

Sodium hydroxide solution, 8% w/v.

Potassium hydroxide solution, 10% w/v.

Sulphuric acid, 50% and 10% v/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 33% hydrochloric acid saturated with hydrogen sulphide.

Hydrogen sulphide wash solution. 1% sulphuric acid saturated with hydrogen sulphide.

Potassium sulphide-potassium hydroxide wash solution. Dissolve 20 g of potassium hydroxide in 1 litre of water and saturate the solution with hydrogen sulphide. Add 2 g of potassium hydroxide, stir to dissolve, and store in a wash-bottle.

Silver nitrate solution, 1% w/v. Dissolve 1 g of silver nitrate in water, add 5-10 drops of concentrated nitric acid, and dilute to 100 ml with water.

Standardization of potassium bromate solution

Transfer 0.1000 g of pure arsenic trioxide (As_2O_3) (Note 2) to a 400-ml beaker, add 5 ml of 8% sodium hydroxide solution, and swirl the beaker until the oxide has dissolved. Add 50 ml of water and 40 ml of concentrated hydrochloric acid, and dilute the solution to approximately 200 ml with water. Add 5 ml of 10% potassium bromide solution (Note 3) and 4 drops of 0.1% Bordeaux indicator solution (Note 4) and, while stirring, titrate the resulting solution with standard 0.05 N potassium bromate solution until the pink colour just disappears (Note 5). Add 2 drops more of the indicator solution and, if necessary, continue to titrate slowly, and while stirring, to a colourless end-point (Note 6). Correct the result obtained by subtracting that obtained for a blank that is carried through the same procedure (Note 7). Determine the normality of the potassium bromate solution, and calculate the antimony equivalents (mg/ml) of both the 0.05 N and the diluted 0.01 N solutions (1 ml of 0.05 N potassium bromate solution = 3.044 mg of antimony; 1 ml of 0.01 N solution = 0.6088 mg of antimony).

Procedures

In these procedures a reagent blank is carried along with the samples.

A - General procedure

Transfer 0.2-5 g of powdered sample, containing up to approximately 150 mg of antimony, to a dry 300-ml Erlenmeyer flask, and add 12 g of potassium pyrosulphate, 0.5 g of tartaric acid (Note 8), and 15 ml of concentrated sulphuric acid. Heat the mixture, gradually at first, over an open flame, then at the full heat of a Meker burner until decomposition is complete. Continue heating until any free sulphur has been expelled, the carbon from the tartaric acid is completely oxidized, and most, but not all of the excess sulphuric acid has been expelled (Note 9), then swirl the flask to distribute the melt in a thin layer around the bottom and lower sides of the flask. Allow the flask and contents to cool, then add 3 g of tartaric acid and 30 ml of water, heat gently to dissolve the soluble salts and, if necessary, filter the solution (Whatman No. 540 paper) into a 400-ml beaker. Wash the beaker, paper, and residue (Note 10) with small portions of 10% sulphuric acid, and then with hot water to remove the acid.

Place the paper and residue on a watch glass, dry in an oven at 100°C, and transfer the major portion of the residue to a 30-ml porcelain crucible. Transfer the paper to another porcelain crucible, and burn off the paper at a low temperature. Add the ash from the paper to the dried residue and, depending on the amount of the residue, add 1-2 g each of potassium carbonate and powdered sulphur and mix thoroughly. Fuse the mixture at a low temperature, and allow the crucible and contents to cool. Transfer the crucible and contents to a 250-ml beaker, and add approximately 75 ml of water. Heat gently to disintegrate the melt, then remove the crucible after washing it thoroughly with hot water. Filter the solution (Whatman No. 40 paper) into a 400-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the paper and precipitate. Using litmus paper, neutralize the solution approximately with 50% sulphuric acid, add 2 ml in excess, and allow the solution to stand until the resultant sulphides have settled. Filter the solution (Whatman No. 40 paper), wash the beaker, paper, and precipitate with a small amount of water, and discard the filtrate. Dissolve the precipitate, using approximately 5 ml of hot 10% potassium hydroxide solution mixed with 1 ml of 30% hydrogen peroxide, and wash the paper thoroughly with hot water. Collect the solution in the beaker that originally contained the sulphide precipitate, and discard the paper. Add 7 ml of 50% sulphuric acid to the resulting solution and evaporate it to fumes of sulphur trioxide to remove elemental sulphur. Cool, add approximately 10 ml of water, heat gently to dissolve the salts, and add the solution to the initial filtrate.

Evaporate the combined solution to approximately 25 ml, cool, and add 50 ml of concentrated hydrochloric acid. Cool to 15-20°C in an ice-bath, and pass hydrogen sulphide through the solution for 30 minutes. Allow the solution to stand for 1 hour, or longer if only a small amount of precipitate is present, then, using suction and a double filter paper (Whatman No. 40) previously moistened with 33% hydrochloric acid saturated with hydrogen sulphide, filter the solution into a 1-litre beaker. Wash the beaker 3 times with small portions of the 33% hydrochloric acid-hydrogen sulphide solution, then wash the paper and precipitate 6 times with the same solution. Discard the paper and precipitate.

Dilute the filtrate (Note 11) with 4 times its volume of hot water, pass hydrogen sulphide through the solution for 30 minutes, and allow it to stand until the mixed sulphide precipitate has settled. Filter the solution (Whatman No. 40 paper) into a 1-litre beaker (Note 12), and wash the beaker, paper, and precipitate thoroughly with 1% sulphuric acid saturated with hydrogen sulphide until the precipitate is free of chlorides (Notes 13 and 14).

Using a jet of hot water, transfer the bulk of the precipitate to the beaker in which the precipitation was carried out, and wash the paper with 20 ml of hot 10% potassium hydroxide solution (Note 15) followed by hot water. Dilute the resulting solution to approximately 75 ml with hot water, pass hydrogen sulphide through the solution for 10-15 minutes, then add 10 ml of

10% potassium hydroxide solution, stir, and allow the solution to stand until the precipitate has settled. Using the same filter paper, filter the solution into a 300-ml Erlenmeyer flask, and wash the beaker, paper, and precipitate thoroughly with small portions of the potassium sulphide-potassium hydroxide wash solution (Note 16). Discard the paper and precipitate.

Add 15 ml of concentrated sulphuric acid to the filtrate (Note 17), evaporate the solution to fumes of sulphur trioxide, and continue heating until all of the sulphur is destroyed and most, but not all of the excess sulphuric acid has been expelled (Note 9). Swirl the flask to distribute the melt around the bottom and lower sides of the flask, and allow the flask and contents to cool. Add 20 ml of 50% sulphuric acid and 10 ml of water, heat gently to dissolve the melt (Note 18), then add 1 g of sodium sulphite (Note 19) in small portions, boil the solution vigorously for several minutes, and evaporate it to approximately 20 ml. Cool, wash down the sides of the flask with approximately 10 ml of water, and again boil and evaporate the solution to 20 ml to ensure the complete expulsion of sulphur dioxide (Note 20). Cool the resulting solution and add approximately 40 ml of water and 20 ml of concentrated hydrochloric acid. If necessary, warm the solution to 50-60°C (Note 21) to dissolve the salts, and dilute to 200 ml with water. Add 5 ml of 10% potassium bromide solution and 4 drops of 0.1% Bordeaux indicator solution and, depending on the expected antimony content of the sample, proceed with the titration of antimony as described above, using either 0.01 N or 0.05 N potassium bromate solution as required. Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

B - Procedure after the separation of arsenic by distillation

Following sample decomposition by treatment with potassium pyrosulphate and sulphuric acid, or by fusion with potassium carbonate and potassium nitrate, and the separation of arsenic by distillation as the trichloride as described in Procedures A and B (pp 236 and 237, Note 13) of the Volumetric-Distillation-Bromate Method for arsenic, add 3 g of tartaric acid to the solution remaining in the distillation flask (Note 22), shake to dissolve and, if necessary, warm the solution to 50-60°C (Note 21) to dissolve the soluble salts. If necessary (Note 23), filter the solution (Whatman No. 541 paper) into an 800-ml beaker, wash the beaker, paper, and residue with small portions of 10% sulphuric acid, and then with warm water to remove the acid. If an appreciable amount of acid-insoluble residue is present (Note 10), dry the paper and residue, separate and burn off the paper, fuse the combined ash and dried residue with potassium carbonate and sulphur, and treat the melt as described above. Add the resultant solution to the main solution.

Dilute the combined solution (Note 11) to approximately 500 ml with hot water, and pass hydrogen sulphide through the solution for 30 minutes. Add 150-200 ml of hot water and continue to pass hydrogen sulphide through the solution for an additional 15-20 minutes (Note 24). Allow the solution to stand until the precipitate has settled, then proceed with the filtration of the mixed sulphide precipitate, the potassium sulphide-potassium hydroxide separation of antimony, and the subsequent titration of antimony as described above.

Notes

1. If pure dry potassium bromate is employed, standardization of the solution is not necessary.

2. Pure antimony trioxide (Sb_2O_3) can also be used to standardize the potassium bromate solution. However, if this reagent is employed, it should be dissolved in potassium hydroxide solution rather than sodium hydroxide solution-sodium salts of antimony are much less soluble than potassium salts[9]. A 0.1000-g portion of antimony trioxide (i.e., 83.53 mg of antimony) requires 27.44 ml of 0.05 N potassium bromate solution.

3. When a reduced compound is titrated with potassium bromate solution, bromide is formed in the first stage of the reaction, and then reacts with

excess of bromate to yield free bromine (Note 6), according to the following reactions:

$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O$

$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 2H_2O$.

A bromide salt is usually added to the test solution before the titration, or is included in the standard bromate solution so that only the second reaction occurs[10].

4. If Bordeaux indicator is not available, aqueous(0.1-0.2%) solutions of methyl orange and various other irreversible internal oxidation indicator compounds (e.g., Brilliant ponceau 5R, napthol blue black, and fuchsine) can also be employed as internal indicators in the direct titration of arsenic (III) and antimony (III) with potassium bromate in the presence of approximately 20% by volume of hydrochloric acid[10,11]. The colour change at the end-point for methyl orange and the above indicators is from orange, dark red, blue, and reddish-yellow, respectively, to colourless[10].

5. A 0.1000-g portion of arsenic trioxide (i.e., 75.74 mg of arsenic) requires 40.44 ml of 0.05 N potassium bromate solution.

6. Bordeaux and other irreversible indicators (Note 4) are destroyed by the free bromine that is liberated at the end-point (Note 3). With all irreversible oxidation indicators, the destruction of the indicator is often premature-particularly if the solution is not stirred vigorously during the titration - and the colour of the solution fades before the equivalence point of the reaction is reached. As soon as the colour disappears, several more drops of indicator solution should be added. If the end-point has been reached, the additional indicator will be destroyed and the solution will become colourless. If the indicator has been destroyed prematurely, the added indicator will colour the solution, and the titration should be continued to the end-point. Because the end-reaction is slow, the last portion of the potassium bromate solution should be added, drop by drop, and with constant stirring. Another drop of indicator solution can be added at the end-point to ensure that the true end-point has been obtained[10,11].

7. The blank correction, which results from the oxidation of the indicator, is generally equivalent to approximately 0.03 ml of 0.05 N potassium bromate solution.

8. Instead of tartaric acid, a small piece of filter paper (approximately one-eighth of a 9-cm paper), or preferably dry paper pulp can be employed to reduce antimony, and arsenic, if present, to the trivalent state during sample decomposition[1].

9. All of the excess sulphuric acid should not be expelled from the solution. This may result in the formation of basic antimony salts which are relatively insoluble in dilute acid[2]. If all of the sulphuric acid has inadvertently been removed from the solution, add 3-4 ml of concentrated acid, evaporate the solution to dense fumes of sulphur trioxide, then proceed as described.

10. The drying, fusion, and subsequent treatment of the acid-insoluble residue can probably be omitted if only a small amount of residue is present. If an appreciable amount of insoluble material is present, it should be quantitatively transferred to the filter paper and treated as described because it may contain antimony. Residues containing lead sulphate should not be ignored because lead sulphate retains an appreciable amount of antimony[2].

11. If the sample contains an appreciable amount of tin, add 10 g of oxalic acid before the dilution of the filtrate, then dilute with hot water as described, and stir to dissolve the oxalic acid. Tin does not interfere in the titration of antimony (III) with potassium bromate because any tin (II) that may be present in the final solution, after the subsequent mixed sulphide and potassium sulphide-potassium hydroxide separation procedures, is oxidized to the tetravalent state when the solution is evaporated to fumes of sulphur trioxide. The resultant tin (IV) is not reduced to the divalent state with sodium sulphite. However, the presence of a large amount of tin sulphide in the mixed

sulphide precipitate is an unnecessary inconvenience during the filtration and washing of the precipitate[2].

12. If the filtrate is not perfectly clear, the solution should be refiltered.

13. To ensure that all of the antimony has been precipitated as the sulphide, add approximately 100 ml of water to the filtrate and washings, warm to approximately 60°C (Note 21), and pass hydrogen sulphide through the solution for 15-20 minutes. If no further precipitation occurs, discard the solution. If a precipitate forms, allow it to settle, and remove most of the supernatant solution by decantation. Filter the solution through the paper containing the initial precipitate, and wash the beaker, paper, and precipitate as described.

14. The precipitate must be free of chlorides or else some antimony will be lost by volatilization as the trichloride during the evaporation of the final solution to fumes of sulphur trioxide[1,2]. The washings can be tested for the absence of chloride ion by boiling a small portion to expel the hydrogen sulphide, and then adding several drops of 1% silver nitrate solution. The complete removal of chlorides is indicated if a clear solution, or only a very faint opalescence is obtained.

15. Because potassium salts of antimony are considerably more soluble than sodium salts, potassium hydroxide solution, rather than sodium hydroxide solution, should be employed for the subsequent alkali sulphide separation, particularly if a large amount of antimony is present in the mixed sulphide precipitate[8].

16. Some antimony may be retained if the amount of precipitate remaining after the potassium sulphide-potassium hydroxide separation procedure is relatively large. To ensure the complete separation of antimony, transfer the precipitate to the beaker again, wash the paper with 10 ml of hot 10% potassium hydroxide solution, and dilute the solution to approximately 50 ml with water. Pass hydrogen sulphide through the solution for 5-10 minutes, then add 5 ml of the potassium hydroxide solution. Allow the precipitate to settle, proceed as described with the filtration and washing of the precipitate, and collect the filtrate and washings in the flask containing the initial filtrate.

17. After acidification with sulphuric acid, the solution will become opaque because of the precipitation of sulphur. It will eventually become clear again during the subsequent evaporation to fumes of sulphur trioxide.

18. If yellow globules of sulphur are present at this stage, filter the solution (Whatman No. 40 paper) into another Erlenmeyer flask, and wash the flask, paper, and residue with small portions of 10% sulphuric acid. Discard the paper and residue. Evaporate the filtrate to approximately 30-35 ml, then proceed as described.

19. Because evaporation of solutions containing antimony (III) to fumes of sulphur trioxide may result in partial oxidation of the antimony to the pentavalent state, treatment of the solution with sodium sulphite at this stage ensures that all of the antimony will be in the trivalent state prior to the titration with potassium bromate[2,5].

20. High results will be obtained for antimony if the sulphur dioxide is not completely expelled from the solution prior to the titration of antimony (III)[1].

21. The solution should not be boiled or else some antimony may be lost by volatilization as the trichloride[1,2].

22. If the sample taken for the determination of arsenic was known to contain an appreciable amount of antimony, and two distillations of arsenic were carried out, add 3 g of tartaric acid to each of the solutions in the distillation flasks. Proceed with the subsequent filtration and treatment of the acid-insoluble residue, if necessary, and the hydrogen sulphide separation procedure, then filter the resultant solutions through the same filter paper.

23. Filtration of the solution is not necessary if acid-insoluble residue was removed by filtration prior to the distillation of arsenic. If necessary (Note 10), the initial

residue should subsequently be dried and treated as described in Procedure A.

24. Because the exact acid concentration of the sample solution is not known after the distillation of arsenic and subsequent treatment of the acid-insoluble residue, the continued passage of hydrogen sulphide through the solution, after further dilution of the solution with water, ensures that all of the antimony present is precipitated as the sulphide.

Calculations

Normality of potassium bromate solution (N_{KBrO_3})

$$= \frac{\text{Weight of arsenic trioxide (g)}}{0.04946 \times (V - v)}$$

where:

V = volume (ml) of potassium bromate solution required by the arsenic trioxide.

v = volume (ml) of potassium bromate solution required by the blank.

Antimony equivalent (mg/ml) of the 0.05 N potassium bromate solution ($Sb_{EQ0.05}$)

$$= N_{KBrO_3} \times \frac{1}{2} \times 121.8$$

Antimony equivalent (mg/ml) of the 0.01 N potassium bromate solution ($Sb_{EQ0.01}$)

$$= Sb_{EQ0.05} \times \frac{1}{5}$$

% Sb

$$= \frac{(V_S - V_B) \times Sb_{EQ0.05 \text{ or } 0.01}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium bromate solution (0.05 or 0.01 N) required by the sample.

V_B = volume (ml) of potassium bromate solution (0.05 or 0.01 N) required by the blank.

$\%Sb_2O_3 = 1.197 \times \%\ Sb$

$\%Sb_2O_5 = 1.329 \times \%\ Sb$

References

1. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 83-89, 92-94, 101 (1962).
2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 273-282, 284 (1953).
3. Idem, ibid., 477 (1953).
4. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, 586 (1948).
5. L.A. Wooten and C.L. Luke, Ind. Eng. Chem., Anal. Ed., 13, 771 (1941).
6. C.L. Luke, ibid., 16, 448 (1944).
7. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 49-54 (1938).
8. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 67 (1953).
9. J.J. Lingane, "Analytical Chemistry of Selected Metallic Elements", Reinhold Publishing Corporation, New York, pp 18-23 (1966).
10. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol III, pp 501-507, 513-514 (1957).
11. G. Frederick Smith and R.L. May, Ind. Eng. Chem., Anal. Ed., 13, 460 (1941).

DETERMINATION OF ARSENIC IN ORES AND MILL PRODUCTS BY TITRATION WITH POTASSIUM BROMATE AFTER DISTILLATION AS ARSENIC TRICHLORIDE

Principle

This method[1-5] involves the separation of arsenic by distillation as the trichloride from an approximately 8 M hydrochloric acid medium, in the presence of hydrazine dihydrochloride as reductant. Arsenic is determined by titration of the resultant arsenic (III) with potassium bromate in a hydrochloric acid medium, in the presence of Bordeaux as internal indicator.

The corresponding reaction for this process is:

$$BrO_3^- + 3As^{+3} + 6H^+ \rightarrow Br^- + 3As^{+5} + 3H_2O.$$

Outline

Sulphide and low-grade oxide ores and mill products are decomposed by heating with potassium pyrosulphate and sulphuric acid, in the presence of tartaric acid, which reduces arsenic and antimony to the trivalent state. The melt is dissolved in water, and arsenic is ultimately separated from the matrix elements by distillation as the trichloride. The arsenic in the distillate is ultimately titrated with potassium bromate solution.

Refractory sulphide and high-grade oxide ores and mill products are decomposed by fusion with a mixture of sodium carbonate and potassium nitrate, and the melt is dissolved in dilute sulphuric acid. Arsenic, and antimony, if present, are ultimately reduced to the trivalent state with sodium sulphite, and arsenic is separated by distillation and determined as described above.

Discussion of interferences

Antimony, and other elements that are reduced to lower oxidation states under the same general conditions required for the reduction of arsenic (V) (e.g., iron, copper, vanadium, and thallium) interfere in the determination of arsenic because they are subsequently oxidized by the potassium bromate[1,2,4,6].

Arsenic is separated from moderate amounts of antimony, from large amounts of iron, copper, vanadium, and thallium, and from tin, magnesium, aluminum, beryllium, uranium, chromium, bismuth, nickel, cadmium, zinc, cobalt, lead, manganese, thorium, tellurium, mercury, silver, cerium, indium, gallium, rhenium, molybdenum, titanium, tungsten, zirconium, phosphate, silicate, platinum metals, gold, alkaline earths, and rare earths by distillation as the trichloride at a temperature (i.e., vapour temperature) of approximately 105°C[1,2,7-9]. Antimony is partly co-distilled as the trichloride at temperatures greater than 107°C[9,10], and at 105°C, if the amount of antimony present during distillation greatly exceeds that of arsenic[9]. Interference from co-distilled antimony (III) can be eliminated by re-distilling the arsenic from the initial distillate[7,9]. Germanium is quantitatively volatilized as the tetrachloride but it does not interfere in this method[7,9]. Selenium is partly co-distilled and may interfere[9].

Range

The method is suitable for samples containing more than approximately 0.01% of arsenic.

Apparatus

Apparatus for the distillation of arsenic. Illustrated in Figure 1. Leakage in the apparatus is minimized by using ground-glass and ball and socket joint connections wherever possible, and by lubricating these connections and all stopcocks with silicone stopcock grease. Rubber stoppers and rubber tubing should not be employed in the construction of the apparatus because they are attacked by the hot, acid vapour during the distillation step, and because they partly absorb the volatilized arsenic trichloride[7].

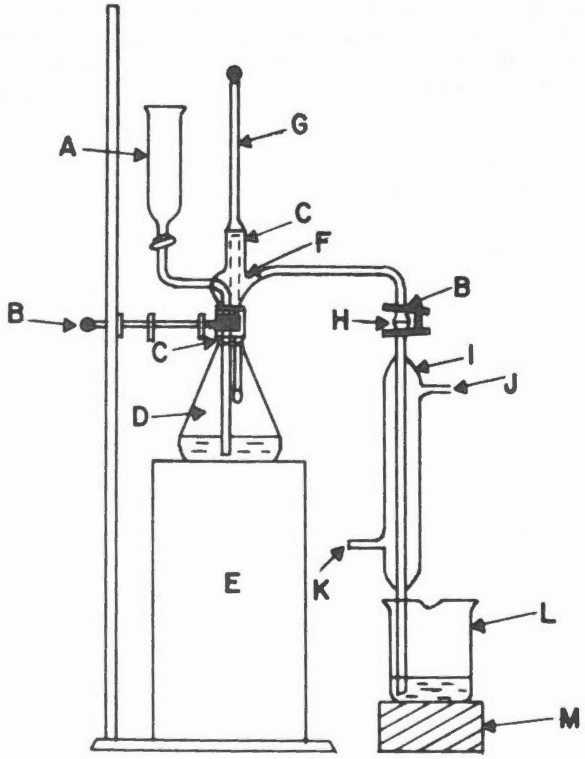

FIGURE 1. Apparatus for the distillation of arsenic

A - Funnel for the addition of acid (approximately 100 ml capacity).
B - Clamp.
C - Ground-glass joint.
D - Distillation flask (300-ml Erlenmeyer-type).
E - Heating element.
F - Distillation head.
G - Partial-immersion thermometer (range -20 to + 150°C).
H - Ball and socket joint.
I - Condenser.
J - Water-outlet.
K - Water-inlet
L - Collecting beaker (400-ml).
M - Block of wood.

Reagents

Standard potassium bromate solutions, 0.05 and 0.01 N. Prepare as described in the Volumetric-Bromate Method for antimony (p 228).

Bordeaux indicator solution, 0.1% w/v. Store in a dropping bottle.

Potassium bromide solution, 10% w/v.

Sodium carbonate-potassium nitrate fusion mixture, 50% each by weight.

Sulphuric acid, 50% and 5% v/v.

Standardization of potassium bromate solution

Standardize the solution against pure arsenic trioxide as described in the Volumetric-Bromate Method for antimony (p 228). Correct the result obtained by subtracting that obtained for a blank that is carried through the same procedure. Determine the normality of the potassium bromate solution, and calculate the arsenic equivalents (mg/ml) of both the 0.05 N and the 0.01 N solutions (1 ml of 0.05 N potassium bromate solution = 1.873 mg of arsenic; 1 ml of 0.01 N solution = 0.3746 mg of arsenic).

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Sulphide and low-grade oxide ores and mill products

Transfer 0.2-5 g of powdered sample, containing up to approximately 100 mg of arsenic, to a dry 300-ml Erlenmeyer distillation flask, and add 12 g of potassium pyrosulphate, 0.5 g of tartaric acid (Note 1), and 15 ml of concentrated sulphuric acid. Heat the mixture, gradually at first, over an open flame, then at the full heat of a Meker burner until decomposition is complete. Continue heating until any free sulphur has been expelled, the carbon from the tartaric acid is completely oxidized, and most, but not all of the excess sulphuric acid has been expelled (Note 2), then swirl the flask to distribute the melt in a thin layer around the bottom and lower sides of the flask. Allow the flask and contents to cool, then add approximately 30 ml of water, and boil the resulting solution for 10-15 minutes to expel any sulphur dioxide that may be present (Note 3). Cool and, if an appreciable amount of insoluble material is present (Note 4), filter the solution (Whatman No. 541 paper) into another distillation flask, and wash the flask, paper, and residue thoroughly with small portions of 5% sulphuric acid (Note 5) followed by hot water. Discard the paper and residue (Note 6). Re-evaporate the solution to approximately 30 ml, cool, and add 4 or 5 glass beads and 1 g each of potassium bromide (Note 7) and hydrazine dihydrochloride (Note 8).

Connect the flask to the distillation head (Figure 1), and start a flow of cold water through the condenser. Place a graduated 400-ml beaker containing 100 ml of cold water (Note 9) under the condenser and, using a block of wood of suitable size, adjust the height of the beaker so that the lower outlet end of the condenser dips well beneath (approximately three-quarter inch) the surface of the water. Add 75 ml of concentrated hydrochloric acid to the funnel, open the stopcock in the funnel, and allow the acid to flow into the distillation flask. Leave the stopcock open, and gradually heat the contents of the flask to the boiling point. Continue heating, at such a rate that the temperature of the vapour remains constant at, but does not exceed 105 ± 1°C (Note 10), until the volume of the solution in the collecting beaker has increased by approximately 40 ml.

Close the stopcock in the funnel, add 25 ml of hot, nearly boiling concentrated hydrochloric acid to the funnel, and slowly, in approximately 5-ml increments (Note 11), add the acid to the distillation flask. Continue the distillation as described above until the volume of the solution in the collecting beaker has increased by approximately 25 ml. Again add 25 ml of hot concentrated hydrochloric acid, distil until a second 25-ml portion of distillate has been collected, then disconnect the condenser from the distillation head, wash the inner part and the outside tip with a small amount of water, and collect the washings in the collecting beaker (Notes 12-14).

Add 10 ml of concentrated hydrochloric acid, 5 ml of 10% potassium bromide solution, and 4 drops of 0.1% Bordeaux indicator solution to the distillate and, depending on the expected arsenic content of the sample, proceed with the titration of arsenic as described in the Volumetric-Bromate Method for antimony (p 228), using either 0.01 N or 0.05 N potassium bromate solution as required. Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

B - Refractory sulphide and high-grade oxide ores and mill products

Transfer 0.2-2 g of powdered sample to a 50-ml nickel crucible, and add a four-fold weight excess of 50% sodium carbonate-50% potassium nitrate fusion mixture (Note 15). Mix thoroughly, and cover the mixture with an additional 2 g of the fusion mixture. Cover the crucible with a nickel cover, heat the contents gradually over a low flame (Note 16), then fuse over a blast burner, and keep the melt at red heat for several minutes to ensure complete sample decomposition (Note 17). Cool, transfer the crucible and cover to a 400-ml beaker, and add approximately 100 ml of water. Heat gently to disintegrate the melt, then remove the crucible and cover after washing them thoroughly with hot water. Neutralize the solution approximately with 50% sulphuric acid, add 15 ml in excess, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool, add approximately 25 ml of water, heat gently to dissolve the soluble salts and, if an appreciable amount of insoluble material is present, filter the solution (Whatman No. 541 paper) into a 300-ml distillation flask. Wash the beaker, paper, and residue thoroughly with small portions of 5% sulphuric acid (Note 5) followed by hot water, and discard the paper and residue (Note 6).

Evaporate the resulting solution to approximately 30 ml, and add 2 g of sodium sulphite in small portions. Boil the solution vigorously for several minutes and evaporate it to approximately 20 ml. Cool, wash down the sides of the flask with water, and boil and evaporate the solution to 20 ml again to ensure the complete expulsion of sulphur dioxide (Note 3). Dilute the solution to approximately 30 ml with water, cool, add 4 or 5 glass beads and 1 g each of potassium bromide and hydrazine dihydrochloride, and proceed with the distillation and subsequent titration of arsenic as described above.

Notes

1. Instead of tartaric acid, a small piece of filter paper (approximately one-eighth of a 9-cm paper), or preferably dry paper pulp can be employed to reduce arsenic, and antimony, if present, to the trivalent state during sample decomposition.

2. Loss of arsenic may occur if the sample solution is fumed too violently at this stage[1]. If all of the sulphuric acid has inadvertently been removed from the solution, add 3-4 ml of concentrated acid, evaporate the solution to fumes of sulphur trioxide, then proceed as described.

3. Incomplete expulsion of sulphur dioxide will cause high results for arsenic because of the co-distillation and subsequent titration of the sulphur dioxide with the potassium bromate solution[9].

4. Large amounts of acid-insoluble material should be removed by filtration at this stage to prevent "bumping" during the distillation step. If free sulphur (yellow globules) was not completely destroyed during the sample decomposition procedure, it should also be removed by filtration. High results will be obtained for arsenic if volatile sulphur compounds (e.g., sulphur dioxide) (Note 3) are formed during the distillation step.

5. The total sulphuric acid content of the solution should not exceed approximately 10 ml at this stage[1,7,9].

6. If antimony is to be determined in the solution remaining in the distillation flask after the separation of arsenic by distillation as the trichloride (Note 13), the acid-insoluble residue should be quantitatively transferred to the filter paper and reserved for the determination of antimony, if an appreciable amount is present, or if it contains lead sulphate.

7. The presence of potassium bromide in the solution during the distillation procedure aids the reduction of arsenic[10], and presumably reduces the time required for the complete distillation of arsenic[2].

8. Hydrazine sulphate can also be employed to reduce arsenic to the trivalent state. However, if this reducing agent is employed, care must be taken that the contents of the distillation flask are not evaporated to dryness, or to near dryness during the distillation step because it decomposes to yield sulphur dioxide which will subsequently be titrated by the potassium bromate (Note 3)[2].

9. If the sample contains an appreciable amount of arsenic, the solution in the collecting beaker should be cooled in an ice-bath during the distillation step to prevent incomplete absorption of the arsenic trichloride[9].

10. If the temperature of the vapour exceeds 107°C, antimony trichloride will co-distill to a certain extent. The temperature of the solution in the distillation flask can be measured instead of the temperature of the vapour. If this technique is employed, the temperature should not exceed 111-112°C[1,7-9].

11. The slow addition of hot hydrochloric acid is recommended at this stage. If cold acid is added too rapidly, the distillate may "back-up" into the condenser because of the resultant decrease in the temperature of the solution in the distillation flask.

12. If the sample contains considerably more antimony than arsenic, some antimony (several tenths of a mg) will be present in the distillate[7,9] and will cause high results for arsenic. Low results will subsequently be obtained for antimony if it is to be determined in the solution remaining in the distillation flask after the distillation of arsenic (Note 13). In exact work, the co-distilled antimony trichloride can be separated from arsenic by performing a second distillation, as follows:

Transfer the distillate to a second distillation flask, wash the collecting beaker twice with 5-ml portions of concentrated hydrochloric acid, and add the washings to the flask. Add 4 or 5 glass beads and 1 g each of potassium bromide and hydrazine dihydrochloride and, omitting the initial addition of the 75 ml of concentrated hydrochloric acid, proceed with the re-distillation until the volume of the solution in the collecting beaker has increased by approximately 100 ml. Add 75 ml of hot concentrated hydrochloric acid to the funnel and, slowly, in approximately 10-ml increments, add the acid to the distillation flask. Distil until approximately 50 ml more of distillate has been collected. Continue the distillation as described, using two more 25-ml portions of hot concentrated hydrochloric acid, then proceed as described with the subsequent titration of arsenic.

13. The solution remaining in the distillation flask (or both solutions if a double distillation of arsenic has been carried out) (Note 12) can be used for the determination of antimony by the Volumetric-Bromate Method (Procedure B, p 230).

14. Arsenic (III) can also be titrated with standard iodine solution at this stage, using starch solution as internal indicator, after neutralization of the distillate with sodium hydroxide solution, slight acidification of the solution with hydrochloric acid, and the addition of solid sodium bicarbonate[1,2,7,9].

Alternatively, both low (0.0002%) and moderate concentrations of arsenic (up to approximately 3.5%) can be determined spectrophotometrically by the Molybdenum Blue Method (p 41), after dilution of the distillate to a definite volume with water.

15. If antimony is to be determined in the solution remaining after the distillation of arsenic trichloride, potassium carbonate should be employed in the fusion mixture rather than sodium carbonate because potassium salts of antimony are considerably more soluble than sodium salts[9,11]. Alternatively, refractory samples can be fused with sodium peroxide, or with a 50% by weight mixture of sodium peroxide and sodium or potassium carbonate, followed by digestion of the melt in water, acidification of the solution with sulphuric acid as described, and evaporation of the solution to fumes of sulphur trioxide to expel hydrogen peroxide.

16. To avoid possible loss of arsenic by volatilization, the initial heating should be gradual so that the mixed salts will melt and permeate the mixture before sample decomposition occurs[2].

17. Prolonged heating may be necessary to decompose some oxidized ores, particularly those containing lead[2].

Calculations

Arsenic equivalent (mg/ml) of the 0.05 N potassium bromate solution ($As_{EQ0.05}$)

$$= N \times \frac{1}{2} \times 74.92$$

where:

N = normality of the potassium bromate solution.

Arsenic equivalent (mg/ml) of the 0.01 N potassium bromate solution ($As_{EQ0.01}$)

$$= As_{EQ0.05} \times \frac{1}{5}$$

$$\% \text{ As} = \frac{(V_S - V_B) \times As_{EQ0.05 \text{ or } 0.01}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium bromate solution (0.05 or 0.01 N) required by the sample.

V_B = volume (ml) of potassium bromate solution (0.05 or 0.01 N) required by the blank.

$\% As_2O_3 = 1.320 \times \% As$

$\% As_2O_5 = 1.534 \times \% As$

Other applications

The method described in Procedure A can be employed to determine arsenic in lead- and tin-base solder metals, and in various metals and alloys[1,12].

References

1. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 106-111, 114-116, 128-130, 131-133 (1962).

2. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Mines Branch Monograph 866, Method No. As-1, Part III, April (1958).

3. D.J. Kew, M.D. Amos and M.C. Greaves, Analyst, 77, 488 (1952).

4. G. Frederick Smith and R.L. May, Ind. Eng. Chem., Anal. Ed., 13, 460 (1941).

5. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, pp 506-507 (1957).

6. Idem, ibid., pp 513, 518-519, 521, 523 (1957).

7. J.A. Scherrer, J. Res. Natl. Bur. Std., 16, 253 (1936).

8. C.J. Rodden, ibid., 24, 7 (1940).

9. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 70-73, 259-262, 268-269 (1953).

10. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd ed., Interscience, New York, 278 (1959).

11. J.J. Lingane, "Analytical Chemistry of Selected Metallic Elements", Reinhold Publishing Corporation, New York, pp 18-23 (1966).

12. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, pp 263-264, 380-381 (1971).

DETERMINATION OF CALCIUM IN ACID-SOLUBLE AND REFRACTORY SILICATE ROCKS AND MINERALS, CARBONATE ROCKS, CLAY, SHALE, AND IRON, CHROMIUM, TITANIUM, MOLYBDENUM AND SULPHIDE ORES AND MILL PRODUCTS BY THE OXALATE-POTASSIUM PERMANGANATE METHOD

Principle

This method[1] is based on the separation of calcium as the oxalate from a dilute ammonium hydroxide medium, and the dissolution of the precipitate in dilute sulphuric acid. Calcium is determined by titration of the liberated oxalate ion with potassium permanganate, in an approximately 0.6 M sulphuric acid medium, according to the reaction

$$2KMnO_4 + 5CaC_2O_4.H_2O + 8H_2SO_4 \rightarrow 5CaSO_4 + K_2SO_4 + 2MnSO_4 + 13H_2O + 10CO_2.$$

Outline

Following the separation of aluminum or the mixed hydrous oxides (R_2O_3) by double precipitation with ammonium hydroxide as described in the Gravimetric-Ammonium Hydroxide (Procedures A to D, pp 143-145, Note 15) and the Gravimetric-8-Hydroxyquinoline (Procedures A and B, pp 153 and 154, Note 16) Methods for aluminum, the combined filtrates and washings are acidified with hydrochloric acid. After decomposition of the excess ammonium salts, the copper and arsenic group elements, if present, are precipitated as the sulphides from a dilute hydrochloric acid medium and separated from calcium by filtration. Manganese is subsequently separated from calcium by precipitation as the dioxide from an ammoniacal medium. The calcium in the resultant filtrate is ultimately precipitated as the oxalate from a dilute ammoniacal medium, and separated from magnesium, sodium, potassium, lithium, chromium (VI), and vanadium (V) by filtration. After dissolution of the precipitate, calcium is re-precipitated to remove occluded elements, and the precipitate is dissolved in dilute sulphuric acid. The oxalate in the resulting solution is titrated with potassium permanganate solution.

Discussion of interferences

With the exception of magnesium and manganese, and possibly chromium (VI), vanadium (V), and the copper and arsenic group elements, depending on the history of the sample solution, the majority of the elements that interfere in the precipitation of calcium by forming insoluble hydrous oxides will have been previously separated from calcium by one or more of the separation procedures (i.e., mercury cathode electrolysis, cupferron-chloroform extraction, and hydrogen sulphide and ammonium hydroxide precipitations) described in the gravimetric methods for aluminum.

Interference from carbonate, phosphate, and fluoride, which cause low results for calcium because of the formation of insoluble calcium compounds, is avoided during the ammonium hydroxide separation of aluminum and other hydrous oxides by employing carbonate-free ammonium hydroxide for precipitation; by co-precipitating phosphate, when necessary, as ferric phosphate in the presence of excess iron (III); and by preliminary evaporation of the sample solution with sulphuric acid, respectively[2]. Interference from copper and arsenic group elements remaining in the filtrate from the ammonium hydroxide separation step is eliminated by separating these elements from calcium by precipitation as the sulphides.

Strontium causes high results for calcium because it is co-precipitated as the oxalate[1,2]. The rare earth elements are also precipitated as oxalates in dilute ammoniacal media, but these elements do not interfere because they are precipitated as the hydrous oxides and separated from calcium during the ammonium hydroxide separation step[2].

Magnesium, manganese, and barium interfere because they form oxalates that are partly occluded by the calcium oxalate precipitate[1-3]. Magnesium forms a strong oxalate complex in ammoniacal media and, unless an excess of ammonium oxalate is present during the initial precipitation of calcium, may interfere by combining with, and/or reducing the excess of oxalate required for the complete precipitation of the calcium. Interference from moderate amounts of magnesium (less than, or approximately equal to the amount of calcium present) is eliminated by precipitating the calcium initially in the presence of a considerable excess of ammonium oxalate, and by re-precipitation. Interference from amounts that are slightly greater than the amount of calcium present can be minimized by a third precipitation[2]. The method is not applicable to samples containing small amounts of calcium and inordinately large amounts of magnesium[2]. Manganese is separated from calcium by oxidizing it to the dioxide with ammonium persulphate in a weakly acid medium, and subsequently occluding the dioxide with the hydrous oxide of zirconium in a weakly ammoniacal medium[1,4]. If sulphuric acid is employed at any stage prior to the ammonium hydroxide separation of aluminum and other hydrous oxides, barium will not be present in the filtrate employed for the determination of calcium, because of its precipitation as the insoluble sulphate and subsequent removal by filtration. Interference from small amounts of barium (up to approximately 5 mg), and from vanadium, chromium, sodium, potassium, and lithium, which are partly occluded by the precipitate, is eliminated by re-precipitating the calcium.

Large amounts of sulphate may cause low results for calcium because of the occlusion of calcium sulphate[1,3], but moderate amounts may be present without producing appreciable error in the calcium result[4]. Incomplete removal of the excess ammonium oxalate from the calcium precipitate will cause high results for calcium.

Range

The method is suitable for samples containing more than approximately 0.5% of calcium.

Reagents

Standard potassium permanganate solution, 0.1 N. Dissolve 3.1606 g of potassium permanganate in 1 litre of freshly boiled and cooled water, and allow the solution to stand for several days. Filter the solution, without washing, through glass-wool or a sintered-glass crucible of fine porosity to remove manganese dioxide. Store in a dark-coloured, glass-stoppered bottle (Note 1).

Zirconium solution, 1.4% w/v. Dissolve 10 g of zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) in approximately 80 ml of water containing 2 ml of concentrated hydrochloric acid, and allow the solution to stand overnight. Filter the solution (Whatman No. 42 paper) into a 200-ml volumetric flask, dilute to volume with water and mix.

Ammonium oxalate solution, 6% w/v. Prepare fresh as required, and heat to 70-80°C and filter before use.

Silver nitrate solution, 1% w/v. Dissolve 1 g of silver nitrate in water, add 5-10 drops of concentrated nitric acid, and dilute to 100 ml with water.

Methyl orange indicator solution, 0.02% w/v.

Ammonium hydroxide, 50% v/v.

Hydrochloric acid, 50% and 5% v/v.

Sulphuric acid, 10% v/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% hydrochloric acid saturated with hydrogen sulphide.

Ammonium nitrate wash solution, 2% w/v.

Ammonium oxalate wash solution, 0.1% w/v.

Standardization of potassium permanganate solution

Transfer 0.3000 g of pure sodium oxalate (dried at 105°C for 1-2 hours) to a 300-ml Erlenmeyer flask containing 50 ml of 10% sulphuric acid and approximately 100 ml of water (previously boiled for 10 minutes and cooled to room temperature), and swirl the flask until the oxalate has dissolved. Heat the resulting solution to 70-80°C, and slowly (Note 2) titrate with standard potassium permanganate solution until a faint pink colour is obtained which persists for approximately 30 seconds (Note 3). Correct the result obtained by subtracting that obtained for a blank that is carried through the same procedure (Note 4). Determine the normality of the potassium permanganate solution, and calculate the calcium equivalent (mg/ml) (1 ml of 0.1 N potassium permanganate solution = 2.004 mg of calcium).

Procedure

Following the separation of aluminum or the mixed hydrous oxides (R_2O_3) by precipitation with ammonium hydroxide (Note 5) as described in Procedures A to D (pp 143-145, (Note 15) of the Gravimetric-Ammonium Hydroxide Method, and Procedures A and B (pp 153 and 154, Note 16) of the Gravimetric-8-Hydroxyquinoline Method for aluminum, neutralize the combined filtrates and washings obtained after the double ammonium hydroxide separation with concentrated hydrochloric acid. Add 4 or 5 drops in excess and, if necessary, evaporate the solution to approximately 400 ml. If the sample contains more than approximately 100 mg of calcium, transfer the solution to a 500-ml volumetric flask, dilute to volume with water (Note 6), mix, and then transfer a suitable aliquot (up to 200 ml), containing approximately 40-80 mg of calcium, to a 600-ml beaker (Note 7). Evaporate the initial solution or, if necessary, the aliquot of the solution (Note 8) to approximately 150 ml. Add 60 ml of concentrated nitric acid and 20 ml of concentrated hydrochloric acid, cover the beaker, and heat gently until the vigorous reaction ceases. Remove the cover, and evaporate the solution to approximately 100 ml. Add 30 ml of concentrated nitric acid and 10 ml of concentrated hydrochloric acid, cover the beaker, and heat the solution again until the reaction ceases. Remove the cover, wash down the sides of the beaker with water, and carefully evaporate the solution to dryness (Note 9). Add 8 ml of concentrated hydrochloric acid and approximately 100 ml of water to the residue, and heat gently until the solution is clear.

If the copper and arsenic group elements were not previously removed by precipitation with hydrogen sulphide, or if a mercury cathode separation was not carried out (Note 10), dilute the solution to approximately 200 ml with water, and heat it to the boiling point. Pass hydrogen sulphide through the solution for approximately 30 minutes, then filter it (Whatman No. 32 paper) into a 600-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hydrogen sulphide wash solution. Discard the paper and precipitate. Boil the filtrate to expel hydrogen sulphide, and evaporate the solution to approximately 100 ml. If necessary, filter the solution to remove coagulated sulphur, and evaporate it to 100 ml again.

Add 1 ml of 1.4% zirconium solution and approximately 0.1 g of dry paper pulp to the initial hydrochloric acid solution of the sample, or to that obtained after the hydrogen sulphide separation step. Using universal indicator paper, add concentrated ammonium hydroxide, by drops, until the solution is slightly ammoniacal, then add 50% hydrochloric acid, by drops, until the solution is just barely acidic (Notes 11 and 12). Add 1 g of ammonium persulphate, stir to dissolve, and heat the solution in a hot water-bath for 20 minutes. Add 1 ml of concentrated ammonium hydroxide, heat the solution for an additional 5 minutes, and immediately filter it (Whatman No. 541 paper) into a 600-ml beaker. Wash the beaker 3 times with hot 2% ammonium nitrate solution, then wash the paper and precipitate 10 times with the same solution (Note 13). Discard the paper and precipitate. Boil the filtrate vigorously to decompose the excess ammonium persulphate, and dilute the solution to approximately 200 ml with water.

Add 5 ml of concentrated hydrochloric acid, several drops of 0.02% methyl orange solution, and 50 ml of hot, filtered 6% ammonium oxalate solution to the resulting solution. Heat the solution almost to the boiling point and, while stirring vigorously, slowly add 50% ammonium hydroxide, by drops, until the indicator changes colour. Add approximately 1 ml in excess, stir, and heat the solution almost to the boiling point again (Note 14), then allow it to stand at room temperature for 2-3 hours (Note 15). Filter the supernatant solution (9 cm Whatman No. 40 paper) into an 800-ml beaker, and retain as much of the precipitate as possible in the original beaker. Wash the precipitate in the beaker 3 or 4 times, by decantation, with cold 0.1% ammonium oxalate solution. Filter the washings through the paper, then wash the paper 3 or 4 times with the ammonium oxalate solution.

Wash down the sides of the beaker containing the calcium oxalate precipitate with hot 5% hydrochloric acid, add 2 ml of concentrated hydrochloric acid, and heat the solution to the boiling point to dissolve the precipitate. Place a 250-ml beaker under the funnel and pour the hot solution through the filter paper. Wash the beaker thoroughly with hot 5% hydrochloric acid and pour the washings through the paper. Wash the paper thoroughly, including the inside flap, with the hot acid solution, then remove and discard the paper, and wash the funnel once or twice with the acid solution.

Dilute the resulting solution to 100-125 ml with water, and add several drops of 0.02% methyl orange solution and 10 ml of hot, filtered 6% ammonium oxalate solution. Re-precipitate the calcium as described above, and allow the solution to stand for at least 4 hours or preferably overnight (Notes 16 and 17). Using suction, filter the solution through a sintered-glass, fine-porosity filtering crucible (Note 18), transfer the bulk of the precipitate to the crucible, and collect the filtrate in a 500-ml Erlenmeyer filtration flask. Wash the beaker thoroughly with small portions of cold water, add the washings to the crucible, then wash the crucible and precipitate with small portions of cold water until the precipitate is free of excess ammonium oxalate and ammonium chloride (Notes 19 and 20).

Place a 300-ml Erlenmeyer filtration flask under the crucible, wash down the sides of the beaker that contained the precipitate with 50 ml of hot 10% sulphuric acid and, slowly, in small portions, add the hot solution to the crucible to dissolve the precipitate. Wash the beaker 3 or 4 times with hot water, add the washings to the crucible, and wash the crucible twice with hot water. Dilute the resulting solution to approximately 150 ml with water, heat it to 70-80°C, and proceed with the titration of oxalate as described above (Notes 21 and 22). Correct the result obtained for the sample by subtracting that obtained for the blank that was carried through the standardization procedure (Note 4).

Notes

1. Potassium permanganate solutions should not be allowed to come into contact with reducing materials (e.g., filter paper or rubber), and should be stored in the dark and protected from evaporation and exposure to reducing vapours or dust. If traces of manganese dioxide are deposited in the solution on standing, it should be re-filtered and re-standardized.

2. The reaction between oxalate ion and potassium permanganate is slow at the beginning of the titration, but as soon as some manganese ion is present the reaction becomes almost instantaneous and the permanganate solution can then be added more rapidly. If the solution cools below 60°C before the end-point is reached it should be reheated to 70-80°C before completing the titration[1].

3. A 0.3000-g portion of sodium oxalate requires 44.77 ml of 0.1 N potassium permanganate solution. The last 0.5-1 ml should be added carefully, by drops, and each drop should be completely reduced (i.e., de-colourized) before the addition of the next drop.

4. The blank correction is generally equivalent to 0.03-0.05 ml of 0.1 N potassium permanganate solution.

5. Low concentrations of calcium (particularly 1% or less) in acid-soluble silicate rocks and minerals, clay, shale, and iron ores and concentrates should preferably be determined by the appropriate atomic-absorption spectrophotometric methods described for these sample materials (pp 3 and 7). Small amounts in chromium, titanium, molybdenum, and sulphide ores and mill products, and

in iron ores and mill products can be determined by atomic-absorption spectrophotometry, after sample decomposition (using a fresh portion of sample) and separation of the matrix elements by the mercury cathode and cupferron-chloroform separation procedures described in the Gravimetric-8-Hydroxyquinoline Method for aluminum (p 151). The resulting solution should subsequently be evaporated to dryness to remove excess sulphuric or perchloric acids, followed by dissolution of the residue in water or a suitable dilute acid. In all of the above methods the resulting solutions can also be used for the determination of magnesium by atomic-absorption spectrophotometry.

6. Dilution of the filtrate is generally necessary only for limestone and dolomite sample solutions.

7. If a small aliquot (e.g., 50 ml) of the sample solution is taken, the subsequent treatment of the solution with nitric and hydrochloric acids to remove ammonium salts is not necessary. In this case, add 8 ml of concentrated hydrochloric acid, dilute to 100 ml with water, and proceed as described with the hydrogen sulphide separation, if necessary (Note 10), and/or the manganese separation.

8. If an aliquot of the solution is taken, approximately half the recommended amounts of nitric and hydrochloric acids can be employed for the destruction of the excess ammonium salts.

9. Extreme care in evaporation is required to avoid "bumping" and subsequent loss of sample, particularly when the solution contains large amounts of sodium salts resulting from the initial fusion of the sample or the acid-insoluble material with sodium carbonate.

10. Separation of the copper and arsenic group elements by precipitation with hydrogen sulphide may be necessary for the filtrates obtained after the ammonium hydroxide separation steps in Procedures B, C, and D of the Gravimetric-Ammonium Hydroxide Method for aluminum (pp 144-145, see Note 7, p 146). This separation step should be applied to the filtrates obtained in Procedure B of the Gravimetric-8-Hydroxyquinoline Method for aluminum (p 154), and also to that obtained in Procedure A (p 153) if iron was separated by methyl isobutyl ketone extraction of its chloro complex (see Note 7, p 156) instead of by electrolysis with a mercury cathode.

11. The filtration of a solution containing colloidal hydrated manganese dioxide is slow, and the separation of manganese is usually incomplete because of the tendency of the precipitate to pass through the filter paper. Separation of manganese by occlusion with the hydrous oxide of zirconium results in rapid filtration of the precipitate and complete separation of manganese. The addition of paper pulp to the solution prevents channelling during the subsequent washing of the precipitate[4].

12. Magnesium, but not calcium, is appreciably occluded by hydrated manganese dioxide (Note 13). Occlusion of magnesium is minimized if manganese is precipitated as the dioxide from an acid solution, but the precipitation of manganese is incomplete. The best separation of manganese is obtained if the precipitation is started in an acid solution, and the solution is subsequently heated, made ammoniacal, and heated again[4].

13. If the sample contains more than approximately 10-15 mg of manganese and, particularly if magnesium is to be determined in the filtrate remaining after the separation of calcium as the oxalate (Notes 12 and 20), the precipitate should be dissolved and manganese should be re-precipitated as follows[1,4]:

Dissolve the precipitate in warm 50% hydrochloric acid containing several mg of sodium sulphite, dilute the solution to 100 ml with water, and re-precipitate the manganese as described. Collect the filtrate and washings in the beaker containing the initial filtrate, evaporate the solution to approximately 200 ml, then proceed as described.

14. The solution should not be boiled or stirred, and the bottom of the beaker should not be scratched at this stage, particularly if an appreciable amount of magnesium is present. The occlusion of magnesium is minimized by

introducing a large excess of ammonium oxalate into the solution to form a super-saturated solution of magnesium oxalate. This super-saturation is decreased by boiling, stirring, and scratching of the beaker and, if a considerable amount of magnesium is present, some magnesium oxalate may precipitate on standing. This post-precipitation of magnesium should be avoided because even a third precipitation of calcium as the oxalate may not be sufficient to remove all of the occluded magnesium from the precipitate[1,3].

15. If the sample contains only milligram-quantities of calcium the precipitate may not appear until several minutes after the solution has been heated. Calcium should not be considered to be absent until the solution has stood for the recommended time[1].

16. If the sample contains more magnesium than calcium (e.g., some dolomites), or more than approximately 5 mg of barium, the solution should be filtered and the precipitate washed as described previously, followed by redissolution of the precipitate and reprecipitation of calcium as described to ensure the complete removal of the occluded magnesium and barium[2]. If magnesium is to be determined in the filtrate remaining after the separation of calcium (Note 20), collect the resultant filtrate and washings in the beaker containing the initial filtrate.

17. If desired, calcium can be determined gravimetrically at this stage by weighing as the oxide, as follows[1,2]:

Filter the solution (9 cm Whatman No. 40 paper) into the beaker containing the initial filtrate (Note 20), transfer the precipitate quantitatively to the filter paper, and wash the paper and precipitate 10 times with cold 0.1% ammonium oxalate solution (not cold water). Transfer the paper and precipitate to a tared 30-ml platinum crucible, partly cover the crucible with a platinum cover and, starting with a cold muffle furnace, burn off the paper at a low temperature, then ignite at approximately 1200°C for 10-15 minutes. Remove the cover for a moment to permit the escape of entrapped carbon dioxide, place the covered crucible in a dessicator containing sulphuric acid or phosphorus pentoxide (not calcium chloride), and weigh as soon as the crucible is cool.

Because calcium oxide is hygroscopic, the ignited residue may gain appreciably in weight if it is left for too long in the dessicator. In a well-covered crucible, the ignited residue does not gain in weight during exposure for up to 1 minute under ordinary atmospheric conditions. However, to avoid possible error resulting from the absorption of water, the first weighing should be a preliminary one, and should be followed by a short re-ignition and a second rapid weighing, in which the balance is previously adjusted to the approximate combined weight of the crucible and residue[1].

Then,

$$\% \text{ CaO} = \frac{\text{Weight of ignited precipitate (g)}}{S} \times 100$$

where:

S = *weight (g) of the sample in the solution or in the aliquot taken.*

The ignited residue should be white. A yellow, light brown, or green colour indicates the presence of manganese, and a grayish-white colour indicates the presence of platinum. If the hydrogen sulphide and manganese separations have been carried out as described, neither of these elements should be present[1]. If the sample contains strontium, the residue will be contaminated with strontium oxide. A correction for strontium can readily be made by dissolving the residue in nitric or hydrochloric acid, diluting the solution to a definite volume with water, and determining the strontium present by atomic-absorption spectrophotometry. The amount of strontium obtained can then be calculated as strontium oxide and subtracted from the weight of the residue.

$\text{SrO (g)} = 1.183 \times \text{Sr (g)}$.

18. Filter paper can also be employed for the final filtration of the precipitate, but oxidation of the paper fibres by potassium permanganate during the titration procedure must be avoided as described in Note 21[1,2].

19. The point at which the precipitate is free of excess ammonium oxalate is difficult to determine, but a reasonable estimate can be made by testing for the absence of chloride ion with silver nitrate solution[3].

The complete removal of chloride ion is indicated when the addition of several drops of 1% silver nitrate solution to a small separate portion of the last washings yields a clear solution (i.e., absence of silver chloride) or only a very faint opalescence. Because calcium oxalate is slightly soluble in water, excessive washing of the precipitate should be avoided.

20. Following the addition of the filtrate and washings to the beaker containing the initial filtrate and washings, the combined solution can be used for the determination of magnesium by the Gravimetric-Pyrophosphate Method (p 182).

21. If filter paper was employed for the second filtration, proceed as follows[1]:

Remove the paper from the funnel with platinum-tipped forceps, and spread the paper out on the upper wall of the beaker that contained the precipitate. Pour 50 ml of hot 10% sulphuric acid through the funnel into the beaker, and wash the funnel with water. Wash the precipitate from the paper with a jet of water, partly fold up the paper, and retain it, out of the solution, on the upper part of the beaker. Heat the solution to dissolve the precipitate, dilute to 150 ml with water, heat to 70-80°C, and titrate rapidly to the first permanent tinge of pink. Add the filter paper to the solution and wash down the sides of the beaker with a small amount of water. Macerate the paper with a stirring rod, re-heat the solution, if necessary (Note 2), and continue the titration to the second end-point.

22. The results obtained by this method are generally slightly low because of the slight solubility of the calcium oxalate precipitate in aqueous media. Up to approximately 0.1 mg of calcium is lost to the filtrate and washings for each precipitation stage[2]. In exact work, if magnesium is not to be determined by the Gravimetric-Pyrophosphate Method in the combined filtrates and washings remaining after the separation of calcium, the small amount of calcium remaining in the filtrate can be determined by atomic-absorption spectrophotometry and added to the result obtained. This necessitates the destruction of the excess ammonium salts and ammonium oxalate in the filtrate, after acidification of the solution with sulphuric acid (approximately 25 or 30 ml of a 50% solution), by two treatments of the solution with 60- and 30-ml portions of concentrated nitric and hydrochloric acids, respectively. This should be followed by evaporation of the solution to dryness, dissolution of the residue in water or dilute hydrochloric or nitric acid, and dilution of the solution to a definite volume with water. If the sample contains only a small amount of magnesium, the resulting solution can also be used for the determination of magnesium by atomic-absorption spectrophotometry.

If magnesium is to be determined in the combined filtrates and washings by the Gravimetric-Pyrophosphate Method, a correction for calcium can also be made by dissolving the ignited magnesium pyrophosphate residue in hydrochloric or nitric acid, and diluting the solution to a definite volume with water, followed by the determination of calcium by atomic-absorption spectrophotometry, and the addition of the amount obtained to the amount of calcium obtained by titration with potassium permanganate.

Calculations

Normality of potassium permanganate solution (N_{KMnO_4})

$$= \frac{\text{Weight of sodium oxalate (g)}}{0.06701 \times (V - v)}$$

where:

V = volume (ml) of potassium permanganate solution required by the sodium oxalate.

v = volume (ml) of potassium permanganate solution required by the blank.

Calcium equivalent (mg/ml) of the potassium permanganate solution (Ca_{EQ})

$$= N_{KMnO_4} \times \frac{1}{2} \times 40.08$$

$$\%Ca = \frac{(V_S - v) \times Ca_{EQ}}{S} \times 100$$

where:

V_S = volume (ml) of potassium permanganate solution required by the sample.

v is as described above.

S = weight (mg) of the sample in the solution or aliquot taken for analysis.

$\% \text{ CaO} = 1.399 \times \% \text{ Ca}$

$\% \text{ CaCO}_3 = 2.497 \times \% \text{ Ca}$

Other applications

This method can be employed to determine calcium in fire-brick, glass, cement, and bauxite.

References

1. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 149-155, 362-369 (1968).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 611-628 (1953).

3. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 345-360 (1948).

4. L.C. Peck, "Systematic Analysis of Silicates", U.S. Geol. Surv. Bull., 1170, pp 30-33 (1964).

DETERMINATION OF CHROMIUM IN CHROMITE, AND CHROMIUM ORES AND MILL PRODUCTS BY POTENTIOMETRIC TITRATION WITH FERROUS AMMONIUM SULPHATE

Principle

This method[1-4] involves the oxidation of chromium to the hexavalent state in a sulphuric-nitric acid medium with ammonium persulphate, in the presence of silver nitrate as catalyst. Chromium is determined by potentiometric (reductimetric) titration of the resultant chromium (VI) with ferrous ammonium sulphate, in a 1 M sulphuric acid medium, according to the reaction

$$Cr_2O_7^{-2} + 6Fe^{+2} + 14H^+ \rightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O.$$

Outline

The sample is decomposed by fusion with sodium peroxide. The melt is digested in water, and the solution is ultimately acidified with sulphuric and nitric acids. The chromium in the resulting solution is oxidized with ammonium persulphate, and ultimately titrated with ferrous ammonium sulphate solution.

Discussion of interferences

Manganese interferes in the determination of chromium because, in the presence of ammonium persulphate and silver nitrate, it is simultaneously oxidized to permanganate which also oxidizes the ferrous ammonium sulphate. Interference from manganese is avoided before the titration step by reducing the permanganate, and any manganese dioxide present, to the divalent state with sodium nitrite; the excess nitrite is destroyed with urea[5].

Vanadium causes high results for chromium because vanadium (V), which is formed during fusion of the sample with sodium peroxide, is quantitatively reduced to the tetravalent state during the titration of chromium. The result obtained can be corrected for co-titrated vanadium by re-oxidizing the vanadium (IV) with potassium permanganate at room temperature, followed by the reduction of the excess permanganate with sodium nitrite, and subsequent re-titration of the vanadium (V); chromium (III) is not re-oxidized under these conditions[5].

Other elements that oxidize iron (II) [e.g., cerium (IV] interfere in this method[1]. Selenium and tellurium may interfere in a similar manner[6]. Iron (III), copper (II), cobalt, nickel, arsenic (V), uranium (VI), beryllium, aluminum, manganese, zinc, phosphate, and moderate amounts of molybdenum, titanium, zirconium, niobium, and tantalum do not interfere[6].

Small amounts of tungsten do not cause appreciable error in the chromium result, but large amounts of hydrated tungsten trioxide, if present during the titration step, cause low results because the precipitate occludes chromium[3]. In the absence of large amounts of coloured ions (i.e., copper, nickel, and cobalt), interference from tungsten can be avoided by complexing the sodium tungstate, formed during digestion of the sodium peroxide melt in water, with hydrofluoric acid, followed by titration of the chromium in the presence of sodium diphenylaminesulphonate as internal indicator[5].

Range

The method is suitable for samples containing more than approximately 7% of chromium, but material containing lower concentrations can also be analyzed if more dilute (e.g., 0.025-0.1 N) ferrous ammonium sulphate solution is employed as titrant.

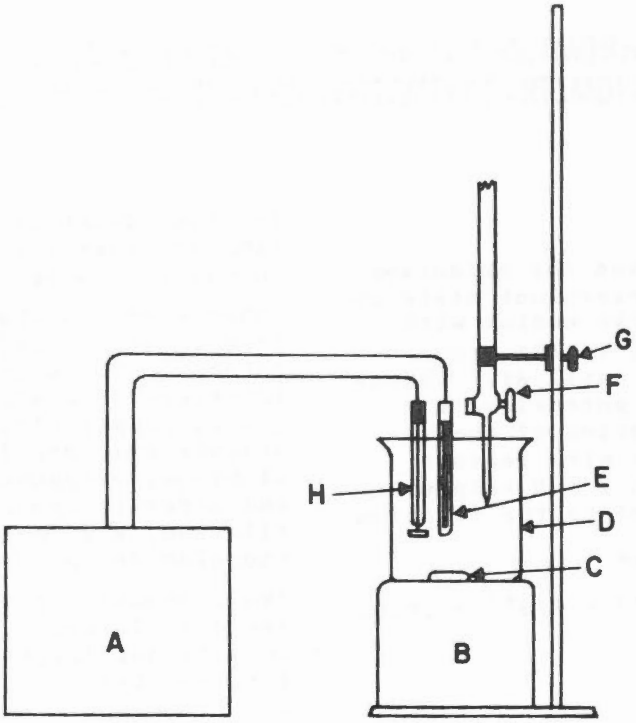

FIGURE 1. Apparatus for the potentiometric titration of chromium

A - pH meter.
B - Magnetic stirrer.
C - Teflon-coated magnet.
D - Titration vessel (600-ml beaker).
E - Calomel reference electrode.
F - Burette (50-ml).
G - Clamp.
H - Platinum electrode.

Apparatus

Apparatus for the potentiometric titration of chromium. Illustrated in Figure 1.

Reagents

Standard ferrous ammonium sulphate solution, 0.2 N. Dissolve 78.432 g of ferrous ammonium sulphate hexahydrate in approximately 700 ml of oxygen-free water, add 100 ml of 50% sulphuric acid, and dilute to 1 litre with oxygen-free water.

Silver nitrate solution, 0.8% w/v.

Ammonium persulphate solution, 25% w/v. Prepare fresh as required.

Potassium permanganate solution, 2% w/v.

Sodium nitrite solution, 0.5% w/v. Prepare fresh as required.

Sulphuric acid, 50% v/v.

Water (oxygen-free). Freshly boiled and cooled water.

Standardization of ferrous ammonium sulphate solution

Transfer 0.1-0.4 g (Note 1) of pure potassium dichromate (dried at 105°C for 1-2 hours) to the titration vessel D (Figure 1), add approximately 100 ml of water, and stir until the dichromate has dissolved. Add 40 ml of 50% sulphuric acid, dilute to approximately 350 ml with water, and titrate the resulting solution potentiometrically with 0.2 N ferrous ammonium sulphate solution (Note 2). Determine the normality of the ferrous ammonium sulphate solution, and calculate the chromium equivalent (mg/ml) (1 ml of 0.2 N ferrous ammonium sulphate solution = 3.466 mg of chromium).

Procedure

Transfer 0.2-0.5 g of powdered sample, containing up to approximately 170 mg of chromium, to a 30-ml iron crucible (Note 3), and add 8 g of sodium peroxide (Note 4). Mix thoroughly and cover the mixture with an additional 1-2 g of sodium peroxide. Cover the crucible with an iron cover, fuse the contents over a blast burner, and keep the melt at red heat for several minutes to ensure complete sample decomposition. Allow the melt to cool for approximately 5 minutes, then transfer the crucible and cover to a 600-ml (covered) beaker containing approximately 150 ml of water. When the subsequent reaction has ceased, remove the crucible and cover after washing them thoroughly with hot water, and boil the solution for approximately 10 minutes to destroy the residual peroxide (Notes 5 and 6). Cool, add 60 ml of 50% sulphuric acid and 5 ml of concentrated nitric acid, and boil the solution until any iron scale from the crucible has dissolved.

Cool the solution to approximately 60°C, add 15 ml of 0.8% silver nitrate solution, 2 drops of 2% potassium permanganate solution, and 10 ml of 25% ammonium persulphate solution, and boil the solution for 5-10 minutes to oxidize the chromium (and manganese) and to destroy the excess persulphate (Note 7). Add 0.5% sodium nitrite solution, by drops, to the boiling solution until the reduction of permanganate and the subsequent decomposition of any precipitated manganese dioxide is complete, then add 1-2 drops in excess. Add 1 g of urea, stir to dissolve, and cool the solution to 20-25°C. If necessary, dilute the solution to approximately 350 ml with cold water, and proceed with the potentiometric titration of chromium (and vanadium, if present) as described above (Note 8).

If the sample contains vanadium, add 2% potassium permanganate solution, by drops, to the titrated solution until a faint pink colour is obtained which persists for 1-2 minutes. Add 0.5% sodium nitrite solution, by drops, until the excess permanganate is reduced, then, without delay, add 1 g of urea, stir to dissolve, and titrate the resulting vanadium (V) with standard ferrous ammonium sulphate solution (Note 9). Correct the initial result obtained by subtracting that obtained for the vanadium.

Notes

1. The reaction between dichromate and ferrous ammonium sulphate is not completely stoichiometric; the result obtained is influenced by acidity, volume of solution, and concentration of dichromate[2,3,7]. For these reasons, and because iron (II) solutions are susceptible to air-oxidation, the ferrous ammonium sulphate solution should be standardized daily just before or preferably after use under the same conditions of acidity and volume prevailing in the analysis. The amount of potassium dichromate taken should be such that the volume of titrant required is approximately the same as that required for the sample. A 0.4000-g portion of potassium dichromate (i.e., 0.1414 g of chromium) requires 40.79 ml of 0.2 N ferrous ammonium sulphate solution.

2. Instead of titrating potentiometrically, oxidized sodium diphenylaminesulphonate can be employed as an internal indicator if the sample does not contain an appreciable amount of coloured ions (i.e., copper, nickel, and cobalt). If this indicator is employed, 5 ml of concentrated phosphoric acid or 3 ml of concentrated hydrofluoric acid should be added, prior to titration, to form a colourless complex with the iron (III) that is formed during titration. During titration the solution is yellowish-brown, at first, then changes to purple-red, and to purple. The colour change at the end-point is from purple to green[5]. With 0.2 N ferrous ammonium sulphate solution as titrant, a correction for an indicator blank is not necessary, particularly if approximately the same volume of iron (II) solution, required to titrate the sample, is employed in the standardization procedure (Note 1)[5]. A correction for an indicator blank is necessary if a more dilute iron (II) solution (e.g., 0.025-0.1 N) is employed as titrant[8].

3. Nickel crucibles, or crucibles made of ingot iron should be employed. Ordinary iron crucibles may contain significant amounts of chromium.

4. Less sodium peroxide (approximately 5 g) is required if about 0.2 g of finely-pulverized sugar charcoal is mixed with the peroxide. Ignition of the charcoal takes place after heating for about 30 seconds, and the crucible will suddenly become a dull red on the outside. The total time required to complete the fusion is about 2 minutes. This extends the life of the crucible because of the reduced time of contact with the molten flux[4].

5. Because peroxide reduces chromium (VI) to the trivalent state in acid solution, the residual peroxide must be destroyed, by boiling, before the solution is acidified. Boiling for 10 minutes is usually sufficient for solutions containing iron, manganese or other active decomposition catalysts (e.g., nickel); at least 30 minutes is required if these elements are absent. Manganese is almost completely converted to the dioxide under these conditions[1].

6. If the sample contains tungsten and only moderate amounts of coloured ions (i.e., copper, nickel, and cobalt), sodium diphenylaminesulphonate (Note 2) can be advantageously employed at this stage as internal indicator in the titration of chromium (and vanadium, if present) (Note 9), after complexing tungsten with hydrofluoric acid, as follows[5]:

Using litmus paper, neutralize the solution approximately with 50% sulphuric acid, add 5 ml of concentrated hydrofluoric acid, then add 40 ml of 50% sulphuric acid and 5 ml of concentrated nitric acid. Boil the solution to dissolve the iron scale from the crucible, and proceed with the oxidation of chromium (and manganese), the reduction of the permanganate with sodium nitrite, and the destruction of the excess nitrite with urea as described. Add 3 ml of concentrated hydrofluoric acid to de-colourize iron (III), titrate the chromium (and vanadium, if present) until a clear green end-point is obtained (Note 2) then, depending on the amount of chromium (III) present (as described below), proceed as described with the re-oxidation and subsequent titration of vanadium (Note 9).

If the above titration procedure is employed in the presence of more than 50 mg of chromium, the solution obtained after the titration of chromium and vanadium should be diluted to a definite volume with approximately 5% sulphuric acid, and an aliquot containing 50 mg or less of chromium should be taken for the re-oxidation and titration of vanadium. More than approximately 50 mg of chromium (III) obscures the end-point of the vanadium titration when sodium diphenylaminesulphonate is employed as internal indicator. The initial result obtained for chromium plus vanadium can be corrected accordingly.

Because hydrofluoric acid is readily volatilized from boiling solutions, more may be required to maintain tungsten in solution when the solution is boiled to dissolve the iron scale and/or to oxidize the chromium. Hydrofluoric acid also maintains titanium, zirconium, niobium, and tantalum in solution during the titration step. Potentiometric titration of chromium is not recommended in the presence of hydrofluoric acid because etching of the glass electrodes will occur.

7. Because the last traces of peroxide are difficult to remove by boiling the alkaline solution (Note 5), re-oxidation after acidification of the solution ensures that all of the chromium is present in the hexavalent state prior to the titration step. Potassium permanganate solution [or a small amount of manganese (II) salt] is added to the solution, prior to oxidation with ammonium persulphate, to ensure that some manganese is present. Complete oxidation of chromium is signalled by the development of the permanganate colour[1].

8. The subsequent procedure for the re-oxidation and re-titration of vanadium should only be omitted if it is definitely known that the sample does not contain vanadium.

9. If the sample contains a moderate amount of vanadium (more than approximately 20 mg), and if cerium, selenium, tellurium, and hydrated tungsten trioxide (which occludes

vanadium) are absent, the vanadium content of the sample can be calculated as follows:

$$\% \text{ V} = \frac{\text{V} \times \text{N}_{\text{Fe(II)}} \times 50.94}{\text{Sample weight (mg)}} \times 100$$

where:

V = *volume (ml) of ferrous ammonium sulphate solution required for the potentiometric titration of the vanadium.*

$\text{N}_{\text{Fe(II)}}$ = *normality of the ferrous ammonium sulphate solution.*

In the absence of the above interfering elements, large amounts of coloured ions (i.e., copper, nickel, and cobalt), and more than approximately 50 mg of chromium (III) (Note 6), sodium diphenylaminesulphonate (Note 2) can also be employed as an internal indicator in the titration of the vanadium[5]. In the presence of tungsten, low results will be obtained for vanadium, unless tungsten is complexed with hydrofluoric acid, prior to the titration step, as described in Note 6. Failure to correct for an indicator blank does not produce an appreciable error in the vanadium result when 0.2 N ferrous ammonium sulphate solution and oxidized sodium diphenylaminesulphonate are employed for the titration[8]. An indicator blank correction can be made as described in Note 7 (p 371) of the Volumetric-Ferrous Ammonium Sulphate Method for vanadium.

If the sample contains only a small amount of vanadium, it should be determined by using the appropriate procedure described in the above method for vanadium (p 365).

Calculations

Normality of ferrous ammonium sulphate solution $[\text{N}_{\text{Fe(II)}}]$

$$= \frac{\text{Weight of potassium dichromate (g)}}{0.04904 \times \text{V}}$$

where:

V = volume (ml) of ferrous ammonium sulphate solution required by the potassium dichromate.

Chromium equivalent (mg/ml) of the ferrous ammonium sulphate solution (Cr_{EQ})

$$= \text{N}_{\text{Fe(II)}} \times \frac{1}{3} \times 52.00$$

$$\% \text{ Cr} = \frac{(\text{V}_\text{s} - \text{V}_\text{v}) \times \text{Cr}_{\text{EQ}}}{\text{Sample weight (mg)}} \times 100$$

where:

V_s = volume (ml) of ferrous ammonium sulphate solution required by the sample.

V_v = volume (ml) of ferrous ammonium sulphate solution required by vanadium, if present.

$\% \text{ Cr}_2\text{O}_3 = 1.461 \times \% \text{ Cr}$

Other applications

This method can be employed to determine chromium in ferro-chromium, and iron ores and mill products[9]. In the absence of an appreciable amount of tungsten, it is also applicable to steel and non-ferrous chromium alloys, after sample decomposition with suitable acids[5,6].

References

1. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 8, pp 324-329 (1963).
2. M. Eppley and W.C. Vosburgh, J. Am. Chem. Soc., 44, 2148 (1922).
3. H.H. Willard and R.C. Gibson, Ind. Eng. Chem., Anal. Ed., 3, 88 (1931).
4. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E342-71, pp 828-830 (1971).
5. H.H. Willard and P. Young, Ind. Eng. Chem., Anal. Ed., 5, 158 (1933).
6. E.C. Pigott, "Ferrous Analysis - Modern Practice and Theory", 2nd ed., Chapman and Hall, Ltd., London, pp 147-155, 159-160, 524, 530-531 (1953).

7. W. Furness, Analyst, 75, 2 (1950).

8. H.H. Willard and P. Young, Ind. Eng. Chem., Anal. Ed., 5, 154 (1933).

9. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, pp 291-292 (1939).

DETERMINATION OF COPPER IN ORES AND MILL PRODUCTS BY THE IODOMETRIC METHOD

Principle

This method[1-4] is based on the formation of cuprous iodide and iodine by the addition of potassium iodide to a weakly acid ammonium hydrogen fluoride or acetic acid solution of copper (II). Copper is determined by titration of the liberated iodine with sodium thiosulphate, in the presence of Thyodene (soluble starch) as internal indicator.

The corresponding reactions for these processes are:

$$2\ Cu^{+2} + 4\ I^- \rightarrow Cu_2I_2 + I_2$$

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI.$$

Outline

"Short iodide" procedure

If molybdenum, small amounts of manganese, and moderate amounts of iron are present, and vanadium, selenium, tellurium, and large amounts of chromium, nickel, cobalt, and acid-insoluble material are absent, the sample is decomposed with hydrochloric, nitric, hydrofluoric, and sulphuric acids. The acid-insoluble material is ultimately removed by filtration, and the filtrate is treated with bromine water to ensure the complete oxidation of arsenic and antimony. The solution is subsequently neutralized with ammonium hydroxide and re-acidified with acetic acid, and iron and molybdenum are complexed with ammonium hydrogen fluoride. After the addition of potassium iodide, the liberated iodine in the resulting solution is titrated with sodium thiosulphate solution.

"Long iodide" procedure

If vanadium, and large amounts of iron, manganese, chromium, nickel, and cobalt are present, the sample is decomposed with hydrochloric, nitric, hydrofluoric, and perchloric acids. Copper and other elements of the copper and arsenic groups (molybdenum, cadmium, bismuth, mercury, lead, tin, arsenic, antimony, gold, and the platinum metals) are subsequently precipitated as the sulphides from a dilute hydrochloric-tartaric acid medium and separated from iron, manganese, vanadium, chromium, nickel, cobalt, tungsten, aluminum, and zinc by filtration. After dissolution of the mixed sulphide precipitate in nitric acid-bromine water solution, nitric acid is removed by evaporation with sulphuric acid.

If selenium and/or tellurium are absent, the resultant solution is ultimately neutralized with ammonium hydroxide and re-acidified with acetic acid. Potassium iodide is added and, if molybdenum is absent, the copper in the resulting solution is determined by titration of the liberated iodine in an acetic acid medium. If molybdenum is present, copper is determined by titration in an ammonium hydrogen fluoride medium.

If selenium and/or tellurium are present, iron solution is added, and selenium, tellurium, and certain other elements (bismuth, arsenic, antimony, and some lead) are coprecipitated as the hydrous oxides, by occlusion with hydrous ferric oxide from an ammoniacal medium, and separated from copper by filtration. After dissolution of the precipitate, the hydrous oxides are re-precipitated to recover occluded copper. Depending on the presence or absence of molybdenum, the copper in the combined filtrates is ultimately determined as described above.

Discussion of interferences

Iron (III), molybdenum (VI), vanadium (V), selenium, tellurium, and oxidizing agents [e.g., nitric acid, nitrogen oxides, chromium (VI), manganese (VII), bromine, and chlorine] interfere in the determination of copper because they also react with potassium iodide to produce free iodine which is subsequently reduced by the sodium thiosulphate[1,3-8]. Arsenic (V) and antimony (V) interfere in a similar manner if the titration is performed in a moderately strong acid medium (i.e., pH less than approximately 3.5)[1,2]. Arsenic (III) and antimony (III) interfere by reacting with the liberated iodine[1,3,6,7]. Large amounts of coloured ions [i.e., chromium (III), nickel, and cobalt] interfere by obscuring the end-point of the titration.

Lead, bismuth and silver react with potassium iodide to form insoluble iodides, but moderate amounts of these elements do not interfere. Interference from large amounts can be minimized by adding a large excess of potassium iodide[6].

Interference from arsenic and antimony is avoided by oxidizing these elements to the pentavalent state with bromine, and by performing the titration in a weakly acidic (i.e., pH greater than 3.5) ammonium hydrogen fluoride (i.e., the "short iodide" procedure) or acetic acid (i.e., the "long iodide" procedure) medium[1,2,7]. Interference from arsenic, antimony, and selenium can be avoided by volatilizing these elements as the bromides from a hydrobromic-perchloric acid medium. Interference from moderate amounts of iron (up to approximately 200 mg) in the "short iodide" procedure, and from large amounts of molybdenum in both the "short" and "long iodide" procedures is avoided by complexing these elements as the fluorides with ammonium hydrogen fluoride[1,4].

Manganese (II), in the absence of iron, does not interfere in either the "short" or "long" iodide procedure. However, in the presence of iron (i.e., the "short iodide" procedure), high results are obtained for copper, presumably because manganese catalyzes and increases the rate of the reaction between iron (III) and iodide ion, and subsequently inhibits the complete complexation of iron (III) by ammonium hydrogen fluoride[1,7]. Several mg of manganese (II), in the presence of iron, do not cause significant error in the copper result[7].

Interference from large amounts of iron, vanadium, chromium, nickel, and cobalt is eliminated, in the "long iodide" procedure, by separating copper from these elements by precipitation as the sulphide from an approximately 0.5 M hydrochloric acid medium. Interference from selenium and/or tellurium (up to approximately 20 mg) is eliminated by separating these elements from copper by coprecipitation as the hydrous oxides with hydrous ferric oxide from an ammoniacal medium[4,9]. Nitrogen oxides, bromine, and chlorine are removed by boiling the solution, or by evaporation with sulphuric acid.

Gold, platinum, and palladium (up to one-tenth the amount of copper present)[4], and zinc, cadmium, mercury, tin, and uranium do not interfere[3,6,7]. Large amounts of ammonium acetate interfere by decreasing the rate of the reaction between copper (II) and potassium iodide[1,6].

Range

The method is suitable for samples containing more than approximately 0.2% of copper.

Reagents

Standard sodium thiosulphate solution, 0.1 N. Dissolve 49.6360 g of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) in approximately 1500 ml of previously boiled and cooled water, and dilute to 2 litres (Note 1).

Standard copper solution (1 ml = 10 mg of copper). Dissolve 1.0000 g of pure copper metal in 25 ml of 50% nitric acid, add 15 ml of 50% sulphuric acid and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool, add approximately 25 ml of water, heat gently to dissolve the salts, cool, and dilute to 100 ml with water.

Thyodene (soluble starch) indicator solution, 5% w/v. Dissolve 5 g each of Thyodene and potassium iodide in water, and dilute to 100 ml. Prepare fresh as required.

Potassium iodide solution, 30% w/v. Prepare fresh as required.

Sodium thiocyanate solution, 40% w/v.

Ammonium hydrogen fluoride solution, 40% w/v. Transfer 100 g of the reagent (NH_4HF_2) to a 250-ml polyethylene beaker, add approximately 200 ml of water, and stir until the reagent has dissolved. Using a polyethylene funnel, filter the solution, if necessary, into a polyethylene bottle marked at 250-ml, and dilute to the mark with water.

Iron solution, 2% w/v. Dissolve 2 g of high-purity iron metal in 15 ml of concentrated hydrochloric acid, add 10 ml of concentrated perchloric acid, and evaporate the solution to dense fumes of perchloric acid. Cool, add approximately 40 ml of water, heat gently to dissolve the salts, cool, and dilute to 100 ml with water.

Bromine water. Water saturated with bromine.

Nitric acid-bromine water solution, 50% each by volume.

Sulphuric acid, 50% and 1% v/v.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 1% hydrochloric acid saturated with hydrogen sulphide.

Ammonium hydroxide wash solution, 2% v/v.

Standardization of sodium thiosulphate solution

Transfer a 10-20-ml aliquot of the standard copper solution to a 300-ml Erlenmeyer flask, and dilute to approximately 30 ml with water. Using litmus paper (Note 2), add sufficient concentrated ammonium hydroxide, by drops, until the solution is just ammoniacal (Note 3), then add concentrated acetic acid, by drops, until the solution is just acidic. Add 4 ml in excess, cool the resulting solution to room temperature in a water-bath, and dilute to approximately 50 ml with water. Add 10 ml of freshly prepared 30% potassium iodide solution (Note 4), mix thoroughly and, while swirling the flask, immediately titrate the solution with standard sodium thiosulphate solution until the brown colour of the liberated iodine has almost disappeared and the solution is pale yellow. Add 5 ml of 40% sodium thiocyanate solution (Note 5), mix, add 5 ml of 5% Thyodene solution, and carefully continue the titration, by drops, until the blue starch-iodine colour has completely disappeared and the solution is pure white (Note 6). Determine the normality of the sodium thiosulphate solution, and calculate the copper equivalent (mg/ml) (1 ml of 0.1 N sodium thiosulphate solution = 6.354 mg of copper) (Note 7).

Procedures

A - "Short iodide" procedure in the presence of molybdenum, several mg of manganese, and up to approximately 200 mg of iron (vanadium, selenium, tellurium, and large amounts of chromium, nickel, cobalt, and acid-insoluble material absent)

Transfer 0.2-1 g of powdered sample, containing up to approximately 200 mg of copper, to a 250-ml Teflon beaker. Add 10 ml of concentrated hydrochloric acid, cover the beaker with a Teflon cover and boil for several minutes. Add 10 ml of concentrated nitric acid and 5 ml of concentrated hydrofluoric acid, and boil until the decomposition of acid-soluble material is complete. Add 10 ml of 50% sulphuric acid, boil for several minutes, remove the cover, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to approximately 3-4 ml to ensure the complete removal of nitric acid. Cool, add approximately 20 ml of water, heat gently to dissolve the soluble salts and, if necessary (Note 8), filter the solution (Whatman No. 541 paper) into a 300-ml Erlenmeyer flask. Wash the beaker, paper, and residue thoroughly with hot 1% sulphuric acid, and discard the paper and residue.

Add 5 ml of bromine water to the filtrate, boil vigorously to expel excess bromine, and evaporate the solution to approximately 30 ml. Using litmus paper (Notes 2 and 9), add sufficient concentrated ammonium hydroxide, by drops, until the solution is just ammoniacal (Note 3), then add concentrated acetic acid, by drops, until the solution is just acidic. Add 5 ml of 40% ammonium hydrogen fluoride solution (Note 10), mix thoroughly and cool the solution to room temperature in a water-bath. Add 10 ml of 30% potassium iodide solution (Note 11), and immediately proceed with the titration of the liberated iodine as described above (Note 12).

B - "Long iodide" procedure in the presence of vanadium, more than approximately 200 mg of iron, and/or large amounts of manganese, chromium, nickel, and cobalt

(a) Selenium and tellurium absent

Following sample decomposition as described above, using 10 ml of concentrated perchloric acid rather than sulphuric acid (Notes 13 and 14), evaporation of the solution to 3-4 ml, and dissolution of the soluble salts in water, transfer the solution and any insoluble material present to a 400-ml pyrex beaker and, without baking, evaporate the solution to dryness. Add 20 ml of water and 7 ml of concentrated hydrochloric acid to the residue, and heat gently to dissolve the soluble salts (Note 15).

Add 5 g of tartaric acid (Notes 16 and 17), dilute to approximately 100 ml with water, and heat the solution to the boiling point. Pass hydrogen sulphide through the solution for 15 minutes to precipitate copper and various other copper and arsenic group elements, and dilute the solution to approximately 150 ml with hot water. Continue passing hydrogen sulphide through the solution for a further 15 minutes to ensure the complete precipitation of copper. Filter the solution (Whatman No. 42 paper) (Note 18) and wash the beaker, paper, and precipitate thoroughly with cold hydrogen sulphide wash solution. Discard the filtrate and washings and, using a jet of hot water, transfer the bulk of the precipitate to the beaker in which the precipitation was carried out. Dissolve the small amount of precipitate remaining on the filter paper, using 20 ml of 50% nitric acid-50% bromine water solution, and wash the paper thoroughly with hot water. Collect the solution in the beaker containing the precipitate, and discard the paper. Add 10 ml of 50% sulphuric acid to the resulting solution and evaporate it to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to 3-4 ml to ensure the complete removal of nitric acid (Note 19). Cool, add approximately 20 ml of water and heat gently to dissolve the soluble salts. If necessary (Note 8), filter the solution (Whatman No. 541 paper) into a 300-ml Erlenmeyer flask, and wash the beaker, paper, and residue thoroughly with 1% sulphuric acid. Discard the paper and residue, and evaporate the resultant solution to approximately 30 ml.

If the sample contains molybdenum, proceed with the neutralization (Note 20), re-acidification, addition of ammonium hydrogen fluoride and potassium iodide solutions, and the subsequent titration of the liberated iodine as described in Procedure A.

If molybdenum is absent, proceed with the neutralization, re-acidification, addition of acetic acid and potassium iodide, and the subsequent titration of the liberated iodine as described under "Standardization of sodium thiosulphate solution".

(b) Selenium and/or tellurium present

Following the separation of copper and various copper and arsenic group elements by precipitation with hydrogen sulphide (Note 21) as described above, and the dissolution of the precipitate in nitric acid-bromine water solution, boil the solution vigorously to expel bromine (Note 22), cool, and add 10 ml of 2% iron solution. Dilute the solution to approximately 150 ml with water, add sufficient concentrated ammonium hydroxide to precipitate hydrous ferric oxide, and add 5 ml in excess. Boil the solution for several minutes to coagulate the precipitate, filter it (Whatman No. 541 paper) into a 600-ml beaker, and wash the beaker, paper, and precipitate thoroughly with 2% ammonium hydroxide.

Using a jet of hot water, transfer the bulk of the precipitate to the beaker in which the precipitation was carried out, add 10 ml of concentrated nitric acid, and heat gently to dissolve the precipitate. Dilute the resulting solution to approximately 150 ml with water, and re-precipitate, filter (using the same filter paper), and wash the hydrous ferric oxide precipitate as described above. Collect the filtrate and washings in the beaker containing the initial filtrate, and discard the paper and precipitate.

Using litmus paper, neutralize the combined filtrates and washings approximately with concentrated hydrochloric acid. Remove the litmus paper, and add 20 ml each of concentrated nitric and hydrochloric acids and 15 ml of

50% sulphuric acid. Cover the beaker, heat gently until the vigorous reaction ceases, then remove the cover, and evaporate the solution to approximately 75 ml. Add 10-15 ml each of concentrated nitric and hydrochloric acids and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again. Cool, wash down the sides of the beaker with water again, and evaporate the solution to 3-4 ml. Cool, add approximately 20 ml of water and heat gently to dissolve the soluble salts. If necessary, filter the solution (Whatman No. 541 paper) into a 300-ml Erlenmeyer flask, and wash the beaker and paper thoroughly with 1% sulphuric acid. Discard the paper. Evaporate the solution to approximately 30 ml and, depending on the presence or absence of molybdenum, proceed with the neutralization (Note 20), re-acidification, and subsequent titration of the liberated iodine as described in Procedure A or under "Standardization of sodium thiosulphate solution", respectively.

Notes

1. Because of the instability of sodium thiosulphate solutions in the presence of thiobacteria, the standard solution should be prepared under reasonably sterile conditions. If a pure reagent and good water are used during preparation, and the solution is kept sterile, it should be stable for several months. If sulphur precipitates during preparation of the solution or during standing, discard it and prepare a fresh solution. The stock flask or bottle should be cleaned thoroughly and disinfected with hot chromic acid cleaning solution[10].

2. Moisten the strip of litmus paper with water, and place it upright in the flask so that approximately one-third of the paper is below the surface of the solution. Because of the dark blue colour of slightly ammoniacal copper solutions, this technique facilitates the subsequent detection of the point at which the solution just becomes ammoniacal.

3. An excess of ammonium hydroxide should be avoided because excessive amounts of ammonium acetate, which is produced during the subsequent re-acidification of the solution with acetic acid, interfere in the final titration of the liberated iodine[1,6].

4. The solution should be titrated immediately after the addition of potassium iodide solution to prevent error resulting from the loss of iodine by volatilization, and from the liberation of iodine by air-oxidation of iodide ion, according to the reaction

$$4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O.$$

The rate of air-oxidation of iodide ion is increased by increased acidity and by sunlight. Consequently, the titration should not be performed in direct sunlight, and solutions containing iodide should be prepared just before use or kept in brown bottles[8]. Alternatively, 3 g of solid potassium iodide can be employed instead of a 30% solution.

5. The addition of sodium thiocyanate solution can be omitted, but a sharper and more accurate end-point is obtained in its presence. The cuprous iodide precipitate, which is formed on the addition of potassium iodide, tends to absorb some iodine which impairs the sharpness of the end-point and introduces some error. The addition of a soluble thiocyanate compound, just before the addition of the Thyodene indicator solution, converts the buff-coloured cuprous iodide to the less-soluble white cuprous thiocyanate, which releases the absorbed iodine and subsequently produces a pure white, instead of a yellowish-white end-point[11].

6. A 20-ml portion of the copper solution (i.e., 200 mg of copper) requires 31.48 ml of 0.1 N sodium thiosulphate solution.

7. Because sodium thiosulphate solutions slowly change in concentration on standing (Note 1), the standard solution should be re-standardized periodically. If the concentration has decreased by more than approximately 1%, a fresh solution should be prepared. Once decomposition has started, it generally proceeds rapidly[10].

8. If only a small amount of acid-insoluble material (e.g., lead sulphate) is present, transfer the solution directly to the Erlenmeyer flask and proceed as described. Open beakers can be employed for the subsequent titration of the liberated iodine, but Erlenmeyer flasks are recommended to minimize error resulting from volatilization of iodine[8].

9. Instead of using litmus paper, the solution can be carefully neutralized with ammonium hydroxide until all of the iron present has been precipitated as the brown hydrous oxide and the solution becomes brownish-green because of the first faint formation of the blue copper-ammonia complex. If this technique is employed, and too much ammonium hydroxide is added, the solution will become deep blue. If this happens, add sufficient dilute (approximately 10%) sulphuric acid to restore the brown-green colour, then add 5 ml of 40% ammonium hydrogen fluoride solution (Note 10), and proceed as described[12].

10. Approximately 2 g of ammonium hydrogen fluoride are required for the complexation of 200 mg of iron. The hydrous ferric oxide precipitate should dissolve completely when the ammonium hydrogen fluoride solution is added and the solution is mixed thoroughly. If it does not dissolve, either too much ammonium hydroxide or insufficient ammonium hydrogen fluoride solution was added. Additional fluoride solution may be necessary if the sample contains an appreciable amount of aluminum and/or molybdenum, or if the solution is still yellow because of un-complexed iron (III). Aluminum forms an insoluble fluoride compound with ammonium hydrogen fluoride which, if present in large amounts, may occlude copper and slow up the titration[1,3,4,7].

11. Because lead, bismuth, and silver react with iodide, more potassium iodide solution may be required if an appreciable amount of these elements are present[6].

12. The blue starch-iodine colour should not return within at least 10-15 minutes after the end-point. A quick return of the colour may be caused by the addition of too much ammonium hydroxide, insufficient ammonium hydrogen fluoride (Note 10), or insufficient acidity (i.e., pH greater than approximately 5.5). The reaction between copper (II) and iodide ion is slow at higher pH values[1,7,13].

13. Perchloric acid, instead of sulphuric acid, is recommended for sample decomposition in this procedure because iron, lead, and particularly chromium perchlorates are considerably more soluble than their sulphates.

14. If the sample contains an appreciable amount of arsenic and/or antimony, these elements will be co-precipitated with copper sulphide in the subsequent hydrogen sulphide separation procedure. Because the presence of a large amount of arsenic and/or antimony sulphides in the mixed sulphide precipitate is an unnecessary inconvenience during the filtration and washing of the precipitate, preliminary removal of these elements by volatilization as the bromides is recommended as follows:

Following evaporation of the sample solution to fumes of perchloric acid (Note 13), cool, and wash down the sides of the beaker with water. Add 10 ml of concentrated hydrobromic acid and evaporate the solution to fumes of perchloric acid. Cool, and wash down the sides of the beaker again. Repeat the hydrobromic acid treatment and subsequent evaporation to fumes, then evaporate the solution to 3-4 ml and proceed as described.

Selenium and tin are also volatilized as the bromides by the above procedure.

15. If much acid-insoluble residue is present, or if the residue is suspected to contain copper, filter the solution (Whatman No. 30 paper) into a 400-ml beaker, and transfer the residue quantitatively to the filter paper. Wash the paper and residue thoroughly with hot water, and treat the paper and residue as follows:

Transfer the paper and residue to a 30-ml porcelain crucible, burn off the paper, and ignite at a low temperature. Fuse the residue with 1-2 g of potassium pyrosulphate, cool, and transfer the crucible and contents to *a 250-ml beaker. Add approximately 75 ml of water, heat gently until the disintegration of the melt is complete, and remove the crucible after washing it thoroughly with hot water. If necessary, filter the solution (Whatman No. 30 paper) into the beaker containing the initial filtrate, and wash the beaker and paper thoroughly with hot water. Discard the paper. Evaporate the solution to approximately 75 ml, then proceed as described.*

16. The addition of tartaric acid may be omitted if vanadium is absent and the sample contains only a small amount of tungsten.

17. If the sample contains an appreciable amount of tin, which was not previously removed by volatilization as the bromide (Note 14), 10 g of oxalic acid may be added at this stage to prevent the subsequent precipitation of tin (IV) sulphide. Tin (IV) does not interfere in the titration of iodine with sodium thiosulphate, but the presence of a large amount of tin sulphide in the mixed sulphide precipitate is an unnecessary inconvenience during the filtration and washing of the precipitate.

18. Because cuprous sulphide is easily oxidized or rendered colloidal, the filter paper should be kept at least two-thirds full of solution during filtration and washing to avoid undue exposure of the sulphide precipitate to air[14].

19. If the sample contains an appreciable amount of iron, vanadium, chromium, nickel, and/or cobalt, evaporate the solution to dryness at this stage. Cool, add 20 ml of water and 7 ml of concentrated hydrochloric acid, and heat gently to dissolve the salts. If necessary (Note 16), add 1-2 g of tartaric acid, dilute the solution to approximately 100 ml with water, and re-precipitate, filter, and wash the copper sulphide as described to remove occluded elements. Following dissolution of the precipitate with nitric acid-bromine water solution, addition of sulphuric acid, and evaporation of the solution to 3-4 ml, proceed as described.

20. Litmus paper must be employed for the neutralization and re-acidification steps at this stage. The procedure described in Note 9 cannot be used because the solution no longer contains iron to function as an internal indicator.

21. If tellurium is absent, and selenium has previously been removed by volatilization as the bromide (Note 14), the subsequent ammonium hydroxide separation procedure is not necessary, and copper can be determined as described in Procedure B (a).

22. If the sample contains an appreciable amount of iron, vanadium, chromium, nickel, and/or cobalt, and re-precipitation of the copper sulphide is necessary (Note 19), add 10 ml of 50% sulphuric acid to the initial solution obtained after dissolution of the mixed sulphide precipitate in nitric acid-bromine water solution. Evaporate the solution to dryness, proceed with the re-precipitation of the copper as described in Note 19, re-dissolve the precipitate in nitric acid-bromine water solution, then proceed as described.

<u>Calculations</u>

Normality of sodium thiosulphate solution (N_{NaTS})

$$= \frac{\text{Weight of copper in aliquot taken (g)}}{0.06354 \times V}$$

where:

V = volume (ml) of sodium thiosulphate solution required by the iodine liberated by the copper.

Copper equivalent (mg/ml) of the sodium thiosulphate solution (Cu_{EQ})

$$= N_{NaTS} \times 63.54 \qquad \text{OR}$$

$$= \frac{\text{Weight of copper in aliquot taken (mg)}}{V}$$

where:

V is as described above.

$$\% \text{ Cu} = \frac{V_S \times Cu_{EQ}}{\text{Sample weight (mg)}}) \times 100$$

where:

V_S = volume (ml) of sodium thiosulphate solution required by the sample.

<u>References</u>

1. B. Park, Ind. Eng. Chem., Anal. Ed., <u>3</u>, 77 (1931).

2. W.R. Crowell, T.E. Hillis, S.C. Rittenberg and R.F. Evenson, ibid., <u>8</u>, 9 (1936).

3. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, pp 368-372 (1939).

4. R.S. Young, "Industrial Inorganic Analysis", John Wiley and Sons, Inc., New York, pp 100-106 (1953).

5. H.W. Foote, J. Am. Chem. Soc., <u>60</u>, 1349 (1938).

6. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 248-249 (1953).

7. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 630-634 (1948).

8. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, pp 199-208, 213, (1957).

9. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 57-58 (1938).

10. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, 230 (1957).

11. H.W. Foote and J.E. Vance, J. Am. Chem. Soc., <u>57</u>, 845 (1935).

12. C.A. Goetz, H. Diehl and C.C. Hach, Anal. Chem., <u>21</u>, 1520 (1949).

13. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, 404 (1962).

14. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 252 (1953).

DETERMINATION OF FLUORIDE IN FLUORSPAR ORES AND MILL PRODUCTS, ACID-SOLUBLE AND REFRACTORY SILICATE ROCKS, CARBONATE ROCKS, CLAY, SHALE, AND FLUORIDE-BEARING MINERALS BY AMPEROMETRIC TITRATION WITH THORIUM NITRATE AFTER DISTILLATION AS HEXAFLUOSILICIC ACID

Principle

Fluoride is determined by amperometric titration with thorium nitrate in an approximately neutral (pH 7-7.5) 0.1 M potassium chloride supporting electrolyte solution[1,2], according to the reaction

$$2H_2SiF_6 + 3Th(NO_3)_4 + 6H_2O \rightarrow 3ThF_4\downarrow + 12HNO_3 + 2H_2SiO_3,$$

after separation by distillation as hexafluosilicic acid from a perchloric acid medium[3,4].

Outline

Fluorspar ores and mill products are decomposed with perchloric acid, and fluoride is separated from the matrix elements by steam-distillation as hexafluosilicic acid. The fluoride in the distillate is ultimately titrated with thorium nitrate solution.

Acid-soluble and refractory silicate rocks, carbonate rocks, clay, shale, and fluoride-bearing minerals are decomposed by fusion with sodium carbonate and the melt is digested in water. The insoluble carbonates are removed by filtration, and the bulk of the silica in the filtrate is precipitated as zinc silicate and separated from soluble sodium fluoride by filtration. The fluoride in the filtrate is ultimately separated from sodium salts, residual silica, aluminum, sulphate, and phosphate by steam-distillation and determined as described above.

Discussion of interferences

Titanium, zirconium, hafnium, iron, aluminum, magnesium, boron, lead, uranium, bismuth, antimony, alkaline earths, and rare earths interfere in the determination of fluoride because they form insoluble or slightly soluble fluoride compounds, or relatively stable complexes with fluoride ion. Anions that form insoluble compounds, soluble non-dissociated compounds, or stable complexes with thorium (e.g., sulphate, sulphite, sulphide, phosphate, carbonate, chloride, bromide, iodide, arsenite, and arsenate) also interfere, depending on the amount present[3,5-12].

Fluoride is separated from most of the above interfering elements and anions, and from various other elements [e.g., cerium (IV), scandium (III), thorium (IV), beryllium, cadmium, chromium (III), cobalt, copper, gallium (III), indium (III), germanium, sodium, potassium, lithium, manganese (II), mercury (II), molybdenum (VI), tungsten (VI), nickel, niobium, tantalum, platinum, rhenium (VII), rhodium (III), selenium (IV), tellurium (IV), silver, thallium (I), tin (II), and zinc] by distillation as hexafluosilicic acid (or a mixture of silicon tetrafluoride and hydrofluoric acid) from a perchloric acid medium at a temperature (i.e., solution temperature) of approximately 135°C[3,4,11,13].

Free sulphur and sulphides, particulaly pyritic sulphur cause high results for fluoride because they are oxidized during sample decomposition and co-distilled as sulphur oxides, which are converted to sulphite and sulphate ions in the distillate, and subsequently react with the thorium nitrate[9,14]. Halides, nitrates, and carbonates are co-distilled as acids and/or free gases, as nitric acid, and as carbon dioxide, respectively[7,9]. Borate is partly co-distilled as boron trifluoride, which interferes because of the resultant formation of non-ionized fluoboric acid in the distillate[9,11]. Phosphate, if present in large amounts, is partly co-distilled (i.e., microgram-quantities) as phosphoric acid, which reacts quantitatively with thorium nitrate[9,10].

Organic compounds, if present in large amounts, may interfere in the distillation procedure by causing an explosive reaction with perchloric acid[3,4]. Large amounts of zirconium, boron compounds, and gelatinous silica produced during sample decomposition retard the volatilization of fluoride[3,4,9,11]. Aluminum also retards the volatilization of fluoride because it forms an acid-soluble aluminum fluoride complex that greatly reduces the partial pressure of fluoride compounds in the gaseous phase above the solution in the distillation flask[13].

Interference from organic compounds, free sulphur, and sulphides can be avoided by igniting the sample at 500-600°C in the presence of calcium oxide as a retentive agent for volatile fluorides[2,7,14], or can be minimized by oxidizing these compounds with potassium permanganate before the distillation step[9]. Chloride, if present in large amounts, can be prevented from co-distilling as the acid or free chlorine by converting it to insoluble silver chloride[4,8]. Co-distillation of phosphate can be minimized by distilling fluoride at a lower temperature (approximately 125°C)[15], or interference from co-distilled phosphate can be eliminated by re-distilling the fluoride from the initial distillate[4,9,10]. Complete distillation of fluoride can be obtained in the presence of moderate amounts of silica, aluminum, zirconium, and boron compounds by collecting 500 ml or more of distillate[3,4,11].

Interference from large amounts of silica, and also from aluminum can be avoided by separating silica from fluoride as insoluble zinc silicate from an alkaline medium, after sample decomposition by fusion with sodium carbonate; the bulk of the aluminum is separated from fluoride as the hydrous oxide under these conditions[3,11,16]. Slightly low results are obtained for fluoride by the above method because a small amount of fluoride is retained by the mixed zinc silicate-hydrous aluminum oxide precipitate. Negative error caused by the retained fluoride can be minimized by recovering the fluoride from the mixed precipitate by distillation. Low results are also obtained if the sample contains both calcium and phosphate, because calcium fluoride, initially present in the sample or formed during the fusion procedure, is not completely converted to soluble fluoride by reaction with sodium carbonate solution. In the absence of phosphate, fluoride present as calcium fluoride is completely converted to soluble fluoride[11].

Interference from carbon dioxide, which is converted to carbonate ion when the distillate is neutralized with sodium hydroxide, is eliminated by removing it, prior to the pH adjustment step, by bubbling nitrogen gas through the distillate.

Large amounts of perchlorate, co-distilled as perchloric acid, and moderate amounts of chloride, bromide, iodide, and nitrate do not interfere in the amperometric titration method[1]. Up to approximately 2 mg of sulphate, and up to approximately 10 mg of borate do not cause significant error in the fluoride result[1,11]. Large amounts of borate interfere[11].

Range

The method is suitable for samples containing more than approximately 0.04% of fluoride. Silicate and carbonate rocks, and clay and shale samples containing lower concentrations can also be analyzed with reasonable accuracy if the distillate is evaporated to a small volume and the whole solution is taken for titration.

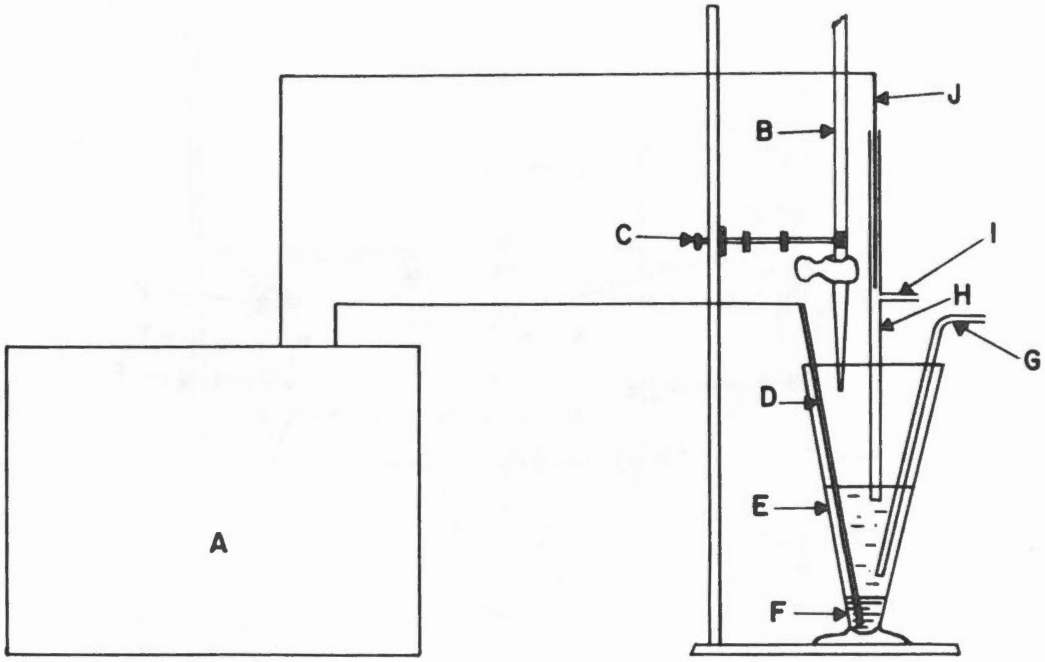

FIGURE 1. Apparatus for the amperometric titration of fluoride

A - Manual polarograph.
B - Burette (10-ml).
C - Clamp.
D - Platinum wire connection to polarograph.
E - Titration vessel (clear plastic 125-ml pharmaceutical graduate).
F - Mercury-pool anode.
G - Plastic nitrogen-inlet tube connected with rubber tubing to the nitrogen tank via a needle valve.
H - Dropping mercury electrode.
I - Dropping mercury electrode mercury-inlet tube connected with rubber tubing to the mercury reservoir.
J - Platinum wire connection to polarograph.

Apparatus

Apparatus for the amperometric titration of fluoride. A typical arrangement of the apparatus is illustrated in Figure 1. The platinum wire connection D to the polarograph consists, with the exception of the tip, of a glass-encased wire surrounded by mercury. Damping of the manual polarograph can be increased, if necessary, by inserting a 4000 microfarad condenser across the galvanometer terminals.

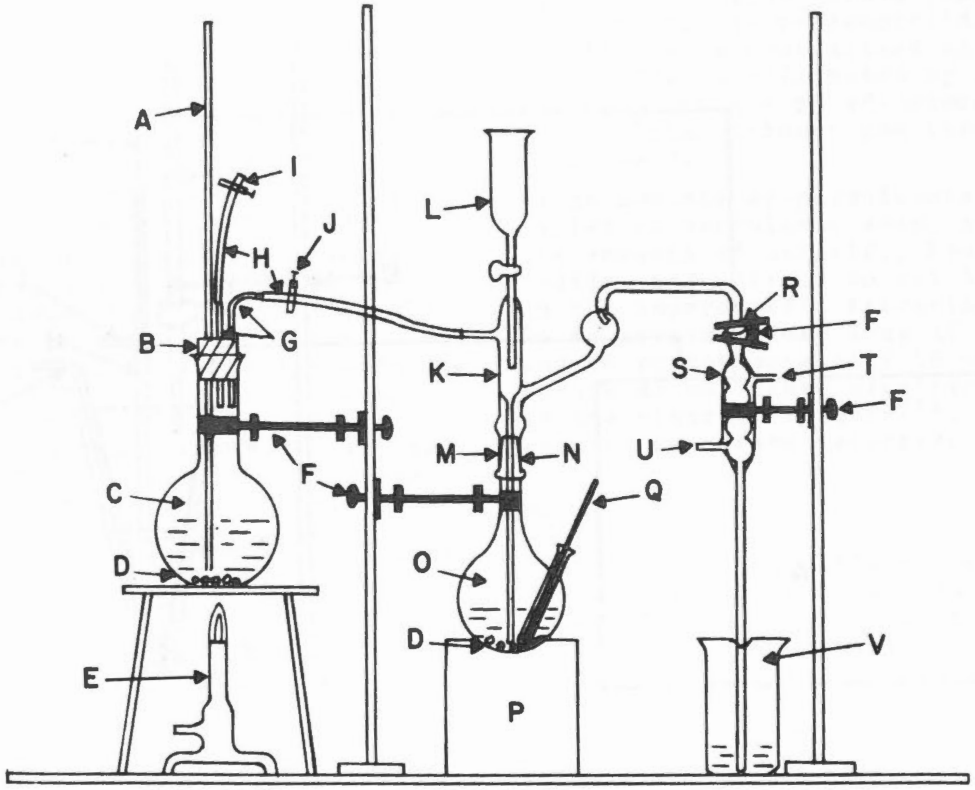

FIGURE 2. Apparatus for the distillation of fluoride

A - Safety pressure-release tube (approximately 2 ft in length).
B - Rubber stopper.
C - Steam-generator flask (1-litre Florence-type).
D - Glass beads.
E - Burner.
F - Clamp.
G - Glass steam-release tube.
H - Rubber tubing.
I - Screw-clamp.
J - Screw-clamp.
K - Distillation head.
L - Funnel for the addition of acid (approximately 75 ml capacity).
M - Ground-glass joint (female-type).
N - Ground-glass joint (male-type).
O - Distillation flask (500-ml modified Claison-type).
P - Heating element.
Q - Thermometer (range 0 to 150°C).
R - Ball and socket joint.
S - Condenser.
T - Water-outlet.
U - Water-inlet.
V - Collecting beaker (600-ml polyethylene).

Apparatus (continued)

Apparatus for the distillation of fluoride. Illustrated in Figure 2. Leakage in the apparatus is minimized by using ground-glass and ball and socket joint connections wherever possible, and by lubricating these connections and all stopcocks with silicone stopcock grease.

Stainless steel beakers. 250-ml.

Reagents

Standard thorium nitrate solution, 0.1 N. Dissolve 13.8055 g of thorium nitrate tetrahydrate $[Th(NO_3)_4.4H_2O]$ in water and dilute to 1 litre. Bubble nitrogen through the resulting solution for 30-40 minutes, prior to use, to remove dissolved oxygen.

Standard thorium nitrate solution, 0.01 N. Dilute 50 ml of the 0.1 N solution to 500 ml with water, and remove oxygen, prior to use, as described above.

Standard fluoride solution (1 ml = 0.7 mg of fluoride). Transfer 0.3868 g of pure sodium fluoride (dried at 110°C for 1 hour), or 0.2389 g of pure lithium fluoride to a 250-ml polyethylene beaker, add approximately 100 ml of water, and swirl the beaker until the fluoride has dissolved. Transfer the resulting solution to a 250-ml volumetric flask and add 12.5 ml of 2 M potassium chloride solution. Dilute to volume with water, mix thoroughly, and immediately transfer the solution to a polyethylene bottle (Note 1).

Potassium chloride solution, 2 M. Dissolve 149 g of the reagent in water, and dilute to 1 litre.

Potassium chloride solution, 0.1 M. Dilute 25 ml of the 2M solution to 500 ml with water.

Sodium hydroxide solution (carbonate-free), 0.1 M. Dissolve 2.000 g of the reagent in water, and dilute to 500 ml. Prepare fresh as required.

Hydrochloric acid, 0.1 M. Dilute 4.28 ml of concentrated hydrochloric acid to 500 ml with water.

Zinc perchlorate solution, 20% w/v. Dissolve 10 g of zinc oxide in 112 ml of concentrated perchloric acid, and add 50 ml of water.

Silver perchlorate solution, 50% w/v. Transfer 10.24 g of silver nitrate to a 250-ml beaker, and add approximately 20 ml of water and 15 ml of concentrated perchloric acid. Swirl the beaker until the salt has dissolved, and evaporate the solution to fumes of perchloric acid. Wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Transfer the resulting solution to a 25-ml volumetric flask, cool, and dilute to volume with water.

Potassium permanganate solution, saturated.

Sodium carbonate wash solution, 2% w/v.

Mercury. Triple-distilled.

Nitrogen (oxygen-free).

Standardization of thorium nitrate solution

Transfer a 25-ml aliquot (Note 2) of the standard fluoride solution to the titration vessel E (Figure 1), add approximately 5 ml of mercury, and bubble nitrogen through the solution for about 5 minutes to remove dissolved oxygen. Insert the platinum wire connection D into the solution so that the tip of the wire is immersed in the mercury pool, then insert the dropping mercury electrode H so that the tip of the capillary tube is approximately one-quarter inch below the surface of the solution. Apply a potential of -1.7 volts to the circuit, adjust the galvanometer setting to the lower end of the scale, stop the nitrogen flow, and record the galvanometer reading. Re-bubble nitrogen through the solution for several minutes to ensure that all dissolved oxygen has been removed (Note 3), then titrate the solution amperometrically with 0.1 N thorium nitrate solution (Notes 4-6). Determine the normality of the thorium nitrate solution, and calculate the fluoride equivalents (mg/ml) of both the 0.1 N and the diluted 0.01 N solutions (1 ml of 0.1 N thorium nitrate solution = 1.900 mg of fluoride; 1 ml of 0.01 N solution = 0.1900 mg of fluoride).

Alternatively, the thorium nitrate solution can be standardized against a sample of fluorspar of known fluoride content, or against pure sodium or lithium fluoride, after carrying these materials through the described distillation procedure (Note 7), and the fluoride equivalent can be determined by direct calculation.

Procedures

In these procedures a blank determination is carried out before the analysis of the sample.

A - Fluorspar ores and mill products

Transfer 0.5-2 g of powdered sample (Note 8), containing up to approximately 250 mg of fluoride, to the distillation flask (Figure 2) (Note 9). Add 8 or 10 soft glass beads approximately 3 mm in diameter (Note 10), and connect the flask firmly to the distillation head. Add approximately 650 ml of water and 8 or 10 glass beads to the steam-generator flask, close the flask with the rubber stopper B, and open the screw-clamp I in the steam-release tube G. Connect the steam-inlet tube of the distillation head to the steam-outlet tube of the steam-generator flask by means of the rubber tube H, close the screw-clamp J, and heat the water in the flask until it is boiling vigorously.

Place a 600-ml polyethylene beaker containing approximately 35 ml of water under the condenser, and adjust the height of the beaker so that the lower outlet end of the condenser dips well beneath the surface of the water. Start a flow of cold water in the condenser, open the stopcock in the funnel L, and add 20 ml of water and 35 ml of concentrated perchloric acid to the distillation flask (Note 11). Close the stopcock, heat the contents of the distillation flask until the temperature of the solution in the flask reaches 135°C (Note 12), then introduce steam into the flask by opening the screw-clamp J and closing the screw-clamp I (Note 13). Maintain the temperature of the solution in the distillation flask at 135 ± 3°C, and the volume at approximately 50 ml by regulating the rate of the steam-flow by means of screw-clamps J and I, and the rate of heating of the sample solution by means of the heating element. Continue the distillation until the volume of the solution in the collecting beaker has increased by approximately 300 ml (Note 14). Disconnect the condenser from the distillation head, wash the inner part and the outside tip with a small amount of water and collect the washings in the collecting beaker, then open screw-clamp I and close screw-clamp J.

Bubble nitrogen through the distillate for 10-15 minutes to remove carbon dioxide, then, using a pH meter, adjust the pH of the solution to 7-7.5 with freshly prepared, carbonate-free 0.1 M sodium hydroxide solution and 0.1 M hydrochloric acid as required. Transfer the solution to a 500-ml volumetric flask, add 25 ml of 2 M potassium chloride solution, dilute to volume with water and mix (Note 15). Transfer a 25-ml aliquot (Note 16) of the resulting solution to the titration vessel, add 5 ml of mercury and, depending on the expected fluoride content of the sample, proceed with the titration of fluoride as described above, using either 0.01 or 0.1 N thorium nitrate solution as required (Notes 17 and 18). Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

B - Acid-soluble and refractory silicate rocks, carbonate rocks, clay, shale, and fluoride-bearing minerals

Transfer 0.5 g of powdered sample (Note 19) to a 30-ml platinum crucible, add 3 g of sodium carbonate (Note 20) and mix thoroughly. Cover the crucible with a platinum cover and heat the mixture in a muffle furnace at approximately 900°C for 30 minutes (Note 21). Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, and allow the crucible and contents to cool. Transfer the crucible and cover to a 250-ml stainless steel beaker (Note 22), add approximately 40 ml of hot water, heat gently in a hot water-bath to disintegrate the melt (Note 23), then remove the crucible and cover after washing them thoroughly with hot water. Filter the resulting solution (Whatman No. 40, 9-cm paper) into a 250-ml stainless steel beaker, and wash the beaker, paper and residue 3 times with approximately 10-ml portions of 2% sodium carbonate solution.

Using a jet of sodium carbonate solution, transfer the bulk of the residue to the original beaker, dilute the mixture to 20-30 ml with the same solution, and boil the solution for several minutes. Filter the solution through the original filter paper, wash the beaker, paper, and residue thoroughly with approximately 10-ml portions of 2% sodium carbonate solution, and collect the filtrate and washings in the beaker containing the initial filtrate. Discard the paper and residue.

By pipette, and while stirring, add 8 ml of 20% zinc perchlorate solution (Note 24) to the combined filtrates, heat the solution to the boiling point, and boil for approximately 1 minute. Filter the solution (Whatman No. 40 paper) into a 250-ml stainless steel beaker, and wash the beaker, paper, and precipitate thoroughly with hot water. Using a jet of hot water, transfer the precipitate to the beaker in which the precipitation was carried out, dilute the mixture to approximately 30 ml with water, and boil the solution for approximately 1 minute. Filter the solution through the same filter paper, wash the beaker, paper, and precipitate thoroughly with hot water (Note 25), and collect the filtrate and washings in the beaker containing the initial filtrate. Discard the paper and precipitate. Evaporate the combined filtrates to approximately 10-15 ml in a hot water-bath and transfer the solution to the distillation flask, using a minimum amount of water to wash the beaker (Note 26). Add 8 or 10 soft glass beads and, omitting the addition of 20 ml of water, proceed with the distillation of fluoride as described above (Note 27).

If the sample contains approximately 35 mg or less of fluoride, bubble nitrogen through the resulting distillate for 10-15 minutes to remove carbon dioxide, then, using litmus paper, neutralize the distillate approximately with freshly prepared, carbonate-free 0.1 M sodium hydroxide solution. Add 3-4 ml in excess, remove the litmus paper, transfer the solution to a large platinum dish or a 600-ml vitreous silica beaker (Note 28), and evaporate the solution to approximately 50 ml in a hot water-bath (Note 29). Cool the solution to room temperature and, using a pH meter, adjust the pH to 7-7.5 with 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solution as required. Transfer the solution to a 100-ml volumetric flask, add 5 ml of 2 M potassium chloride solution, dilute to volume with water and mix. Transfer a 5-25-ml aliquot of the resulting solution (Note 16), containing up to approximately 1.8 mg of fluoride, to the titration vessel. Add 5 ml of mercury, dilute to 25 ml, if necessary, with 0.1 M potassium chloride solution, and proceed with the titration of fluoride as described above, using 0.01 M thorium nitrate solution. Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

If the sample contains more than approximately 35 mg of fluoride, bubble nitrogen through the distillate for 10-15 minutes, adjust the pH of the solution to 7-7.5, and transfer it to a 500-ml volumetric flask. Add 25 ml of 2 M potassium chloride solution, dilute the solution to volume with water, mix, and proceed with the titration of fluoride as described in Procedure A, using 0.1 N thorium nitrate solution.

Notes

1. If the solution is stored in a glass container, etching of the glass will occur because of the reaction of fluoride ion with the silica in the glass.

2. A smaller aliquot of the standard fluoride solution can be employed for the standardization of the thorium nitrate solution but it should be diluted to approximately 25 ml with 0.1 M potassium chloride solution, prior to the titration step.

3. A constant galvanometer reading indicates the absence of oxygen.

4. During the titration, stop the nitrogen flow after the addition of each increment of thorium nitrate solution, and allow the thorium fluoride precipitate to settle for 3-4 minutes before recording the galvanometer reading. Within approximately 2 ml of the end-point (Note 5), add approximately 0.1 ml-increments of the thorium solution, and bubble nitrogen through the solution for approximately 1 minute each time to mix the solution and to remove dissolved oxygen. The galvanometer readings should remain almost constant until the end-point is reached. At the end-point a drop or two of excess thorium nitrate solution will cause a rapid increase in the galvanometer reading. At this point, readings should be taken after the addition of each drop of titrant (Note 6). The height of the mercury column for the dropping mercury electrode should be constant throughout the titration, and the mercury drop time should be approximately 3-4 seconds.

The removal of the dropping mercury electrode from the solution, when nitrogen is bubbled through the solution after the addition of each increment of thorium nitrate solution, will prevent fouling of the mercury drop by the thorium fluoride precipitate. The temperature of the solution influences the amperometric titration of fluoride with thorium nitrate, but titrations can be carried out at room temperature, without a constant temperature-bath, if the temperature change during the titration does not exceed 2 or 3°C[1].

5. A 25-ml portion of the fluoride solution (i.e., 17.5 mg of fluoride) requires 9.21 ml of 0.1 N thorium nitrate solution.

6. Damping does not entirely eliminate the oscillation of the galvanometer needle after the end-point has been reached. Consequently, several readings should be taken and averaged for each added increment of thorium nitrate solution.

7. In careful work, the distillation apparatus can be tested for gas-tightness, following the standardization of thorium nitrate solution against sodium or lithium fluoride, by determining the fluoride content of a standard fluorspar sample of known fluoride content, or of pure anhydrous sodium or lithium fluoride. The theoretical amount of fluoride present in sodium and lithium fluoride is 45.24 and 73.25%, respectively.

8. If the sample contains an appreciable amount of organic material, an explosive reaction with perchloric acid can occur during the subsequent distillation procedure, particularly if the solution is inadvertently evaporated until the perchloric acid is present in concentrated form[3,4]. Organic material, and also free sulphur can be eliminated, before the distillation of fluoride, by covering the sample with calcium oxide (fluoride-free) and heating it at 500-600°C in a silica dish or crucible for approximately 30 minutes. Interference from sulphides can also be eliminated by this method[2,7,14]. Alternatively, organic material, free sulphur, and sulphides can be oxidized, and prevented from interfering during or after the distillation of fluoride, by moistening the sample in the distillation flask with approximately 5 ml of saturated potassium permanganate solution[9].

9. The distillation apparatus should be thoroughly cleaned with hot (approximately 10%) sodium hydroxide solution between successive distillations to remove trace amounts of fluoride ion that are adsorbed on the inner glass surfaces of the apparatus during the distillation procedure[17], and to remove accumulated silica, which tenaciously retains fluoride ion. If the coating of silica is allowed to accumulate, serious errors may occur when the flask is used successively for the analysis of samples containing widely differing quantities of fluoride[7,9]. It is recommended that one distillation flask or group of flasks should be employed for samples containing milligram-quantities of fluoride, and another flask or group of flasks should be used for samples containing large amounts[4].

10. The glass beads supply silica for the formation of hexafluosilicic acid, reduce etching of the distillation flask by fluoride ion, and control superheating and "bumping" during the distillation procedure[3,4]. Hard glass beads should not be employed.

11. If the sample contains an appreciable amount of chloride, add 1 ml of 50% silver perchlorate solution at this stage.

12. Fluoride can be quantitatively distilled from perchloric acid media at temperatures varying from approximately 120 to 150°C, but a temperature of 135 ± 3°C is recommended to prevent excessive co-distillation of perchloric acid. If the sample contains organic material, care should be taken that the temperature of the solution does not rise above 135°C or else an unduly violent oxidizing action may occur (Note 8)[3,4].

13. Optimum distillation of fluoride occurs when the water in the steam-generator flask is boiling vigorously.

14. With most samples containing moderate amounts of fluoride, all of the fluoride is usually collected in the first 150-250 ml of distillate, but the collection of at least 300 ml is recommended to ensure the quantitative distillation of the fluoride. If

the sample contains an appreciable amount of aluminum, zirconium, borate, or gelatinous silica, it may be necessary to collect 500 ml or more of distillate to ensure the complete distillation of the fluoride[4,11]. In this case, depending on the expected fluoride content of the sample, the pH of the distillate can be adjusted to 7-7.5 as described and the solution can be diluted to 1000 ml after the addition of 50 ml of 2 M potassium chloride solution, or the distillate can be concentrated by evaporation, as described in Procedure B, followed by pH adjustment and subsequent treatment as described.

15. If a delay is necessary before the titration of fluoride, transfer the solution to a polyethylene bottle (Note 1).

16. A larger aliquot (e.g., 50-100 ml) of the sample solution can be taken for the titration of fluoride, but longer time intervals are required for the complete removal of dissolved oxygen with nitrogen prior to, and during the titration procedure, and for the settling of the thorium fluoride precipitate (Note 4).

17. Considerable time can be saved if one aliquot of the sample solution is first titrated rapidly to determine the approximate end-point, followed by a second, accurate titration in which all but the last 2 ml of the required volume of standard thorium solution is added, in one stage, at the beginning of the titration procedure.

18. If the fluoride content of the aliquot is approximately 2 mg or less, 0.01 N thorium nitrate solution should be employed for the titration procedure.

19. Fluoride can be determined in fluoride-bearing minerals, that are soluble in perchloric acid and do not contain an appreciable amount of aluminum (e.g., apatite), by the method described in Procedure A. However, in the presence of an appreciable amount of phosphate, the distillation of fluoride should be carried out at a lower temperature (i.e., 120-125°C) to prevent the "carry-over" of phosphoric acid into the distillate[15,16]. Preferably, the distillate collected at 135 ± 3°C should be made alkaline and concentrated to 10-15 ml by evaporation as described in the subsequent procedure, followed by re-distillation of the fluoride to remove the co-distilled phosphoric acid[10,16]. Depending on the fluoride and silica contents (Note 20), fluoride-bearing minerals that are insoluble in perchloric acid, and do not contain an appreciable amount of aluminum and/or silica can be decomposed by fusion with sodium carbonate as described, and analyzed directly (i.e., without prior separation of aluminum and silica) by the method described in Procedure A, after disintegration of the melt in a minimum amount of water, and transference of the resulting mixture to the distillation flask[11,12]. If this method is employed, the addition of 20 ml of water should be omitted; the perchloric acid should be added slowly to the distillation flask; and the solution should be heated gently at the beginning of the distillation step to avoid excessive frothing and possible "carry-over" of the solution into the condenser because of too violent an evolution of carbon dioxide.

If the sample contains both calcium and phosphate, low results will be obtained by this procedure because calcium fluoride, initially present in the sample or formed during the fusion procedure, is not completely converted to soluble fluoride during the subsequent treatment of the sodium carbonate melt with hot water[11]. Probably most of the fluoride, in the calcium fluoride remaining in the insoluble residue obtained after filtration of the solution of the melt, can be recovered by distillation and subsequently determined as described in Note 25.

20. If the sample contains an appreciable amount of fluoride and only a small amount of silica, it may be necessary to add 50-100 mg of pure powdered silica at this stage to obtain complete decomposition of the fluoride-bearing constituent[11].

21. A muffle furnace, started cold, or at a temperature of approximately 500°C, followed by gradual heating to 900°C, is recommended for fusion of the sample to ensure that the mixture is not heated at too high a temperature. Fluoride is not volatilized as

silicon tetrafluoride during fusions with sodium carbonate at temperatures below approximately 1000°C, but appreciable loss occurs at temperatures exceeding approximately 1100°C[11].

22. Vitreous silica, and glass beakers of low boron content, or preferably large platinum dishes can also be employed at this stage. Loss of fluoride occurs if heating or evaporation of alkaline fluoride solutions is carried out in borosilicate glassware, presumably because of partial adsorption of fluoride ion on the surface, and partial reaction of fluoride with the boron in the glass[4,17].

23. To avoid contamination, care should be taken that bottles of hydrofluoric acid are not in the vicinity during heating or evaporation of alkaline fluoride sample solutions.

24. Because an alkaline medium is required for the precipitation of silica as zinc silicate, more zinc perchlorate solution should not be added or else the resultant solution may not be alkaline.

25. Because of its bulk, the zinc silicate precipitate must be thoroughly washed with hot water to avoid too great a loss of fluoride. Some fluoride is usually retained by the voluminous precipitate[11], but this does not cause significant error in the result if the sample contains approximately 2% or less of fluoride. In careful work, particularly with samples of high fluoride content (i.e., fluoride-bearing minerals), most of the fluoride retained by the precipitate can be recovered by distillation, as described in Procedure A, after transferring the precipitate quantitatively to the distillation flask. Following neutralization and evaporation of the resultant distillate to approximately 50 ml, as described in the subsequent procedure, the amount of residual fluoride can be determined, using a 25-ml aliquot of the resultant solution, and added to the result obtained after evaporation and distillation of the fluoride in the filtrate[11].

26. To avoid the addition of too much water to the distillation flask, the final wash of the beaker can be made with the perchloric acid required for the distillation procedure.

27. With silicate rock, carbonate rock, clay, and shale samples, which generally contain only small amounts of fluoride, the collection of approximately 150-200 ml of distillate is usually sufficient for the complete recovery of the fluoride. With fluoride-bearing minerals containing large amounts of fluoride, the volume of distillate recommended in Procedure A should be collected.

28. If necessary, glass beakers of low boron content can also be employed (Note 22).

29. Less than 0.04% of fluoride in silicate and carbonate rocks, clay, and shale can be determined if the solution is evaporated to approximately 5 ml, preferably in a platinum dish, and transferred to the titration vessel with approximately 10 ml of water. Following pH adjustment, addition of 1.25 ml of 2 M potassium chloride solution, and dilution of the solution to approximately 25 ml with water, titrate the resulting solution with 0.01 N thorium nitrate solution as described.

Calculations

Normality of thorium nitrate solution (N_{Th})

$$= \frac{\text{Weight of fluoride in aliquot taken (g)}}{0.019 \times V}$$

where:

V = volume (ml) of thorium nitrate solution required by the fluoride.

Fluoride equivalent (mg/ml) of the 0.1 N thorium nitrate solution ($F_{EQ\ 0.1}$) = $N_{Th} \times 19.00$

OR

$$= \frac{\text{Weight of fluoride in aliquot taken (mg)}}{V}$$

where:

V is as described above.

Fluoride equivalent (mg/ml) of the 0.01 N thorium nitrate solution

$$(F_{EQ\ 0.01}) = F_{EQ\ 0.1} \times \frac{1}{10}$$

$$\%F = \frac{(V_S - V_B) \times F_{EQ\ 0.1\ \text{or}\ 0.01}}{S} \times 100$$

where:

V_S = volume (ml) of thorium nitrate solution (0.1 or 0.01 N) required by the sample.

V_B = volume (ml) of thorium nitrate solution (0.1 or 0.01 N) required by the blank.

S = weight (mg) of the sample in the aliquot taken for analysis.

$\%\ CaF_2 = 2.055 \times \%F$

Other applications

The method described in Procedure A can be employed to determine fluoride in phosphate rock if the distillation of fluoride is carried out at 120-125°C, or if the initial distillate is concentrated by evaporation, followed by re-distillation of the fluoride to remove co-distilled phosphoric acid[10,16].

References

1. A. Langer, Ind. Eng. Chem., Anal. Ed., 12, 511 (1940).
2. A. Hitchen, "The Amperometric Titration of Fluoride with Thorium Nitrate", Dept. of Energy, Mines and Resources, Mines Branch, Extraction Metallurgy Division, Ottawa, Topical Report No. TR-102/52, August (1952).
3. H.H. Willard and O.B. Winter, Ind. Eng. Chem., Anal. Ed., 5, 7 (1933).
4. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 7, pp 238-242, 299-302 (1961).
5. Idem, ibid., pp 259-262 (1961).
6. I.M. Kolthoff and V.A. Stenger, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. II, pp 320-322 (1947).
7. W.M. Hoskins and C.A. Ferris, Ind. Eng.Chem., Anal.Ed., 8, 6 (1936).
8. W.F. Eberz, F.C. Lamb and C.E. Lachele, ibid., 10, 259 (1938).
9. D.S. Reynolds and W.L. Hill, ibid., 11, 21 (1939).
10. H.V. Churchill, R.W. Bridges and R.J. Rowley, ibid., 9, 222 (1937).
11. H.R. Shell and R.L. Craig, Anal. Chem., 26, 996 (1954).
12. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 742-744 (1953).
13. E.J. Fox and W.A. Jackson, Anal. Chem., 31, 1657 (1959).
14. J.I. Hoffman and G.E.F. Lundell, J. Res. Nat. Bur. Std., 20, 610 (1938).
15. E.J. Fox, Anal. Chem., 32, 1530 (1960).
16. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 447-451 (1968).
17. Idem, ibid., pp 250-252 (1968).

DETERMINATION OF TOTAL IRON IN ORES AND MILL PRODUCTS, SLAGS, ACID-SOLUBLE AND REFRACTORY SILICATE ROCKS AND MINERALS, CARBONATE ROCKS, CLAY, AND SHALE BY TITRATION WITH POTASSIUM DICHROMATE AFTER REDUCTION WITH STANNOUS CHLORIDE

Principle

This method[1-3] is based on the reduction of iron to the divalent state with stannous chloride in a hydrochloric acid medium. The excess of the reductant is eliminated by oxidation with mercuric chloride, and iron is determined by titration of the resultant iron (II) with potassium dichromate, in an approximately 0.3 M sulphuric-0.2 M phosphoric acid medium, in the presence of sodium diphenylaminesulphonate as internal indicator.

The corresponding reactions for these processes are:

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2\downarrow$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl \rightarrow 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O.$$

Outline

Ores, mill products, and slags are decomposed with hydrochloric acid in the presence of potassium chlorate as an oxidant (or by treatment with other suitable acids, or by fusion with a suitable flux, depending on the type of sample material). The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate or potassium pyrosulphate, and the melt is dissolved in dilute hydrochloric acid.

> If 2 mg or less of tungsten and 0.5 mg each or less of vanadium, molybdenum, and copper are present, the residual iron in the solution of the melt is precipitated as the hydrous oxide with ammonium hydroxide, and separated from any platinum present by filtration. After dissolution of the precipitate, the resultant solution is added to the initial filtrate. The iron in the resulting solution is ultimately reduced with stannous chloride and titrated with potassium dichromate solution.
>
> If more than the above amounts of any of the above interfering elements are present, the solution of the melt is added to the initial filtrate. Iron is separated from excess amounts of molybdenum and/or copper, and from platinum by precipitation as the hydrous oxide with ammonium hydroxide; from excess amounts of tungsten and/or vanadium, and from molybdenum and platinum by precipitation as the hydrous oxide with sodium hydroxide; or from excess amounts of all of the above elements by both separation procedures. After dissolution of the precipitate, the iron in the resulting solution is determined as described above.

Acid-soluble silicate rocks and minerals, carbonate rocks, clay, and shale are decomposed with hydrofluoric, hydrochloric, and perchloric acids, and the solution is evaporated to fumes of perchloric acid to remove silica and excess hydrofluoric acid. Refractory silicate rocks and minerals are decomposed by fusion with sodium carbonate, the melt is dissolved in dilute perchloric acid, and silica is removed by volatilization as silicon tetrafluoride. The iron in the resulting solutions is ultimately determined as described above, after its separation from any platinum present by precipitation as the hydrous oxide with ammonium hydroxide.

Discussion of interferences

Arsenic, antimony, platinum, gold, molybdenum, tungsten, and uranium interfere in the determination of iron because they are either partly or completely reduced to lower oxidation states with stannous chloride, and are subsequently oxidized by the potassium dichromate[1,4-7]. Vanadium interferes in a similar manner because it is reduced below the tetravalent state; vanadium (IV) does not interfere because of the high redox potential of the vanadium (V)-vanadium (IV) system[8]. Titanium interferes if it is present in solution in the trivalent state prior to the reduction of iron with stannous chloride[1]. Carbonaceous material causes high results for iron because it is partly oxidized by potassium dichromate[6]. Copper causes low results because it catalyzes the air-oxidation of iron (II) to the trivalent state[5,7]. Because of its intense colour in solution, chromium (III), if present in large amounts, may interfere by masking the violet-blue sodium diphenylaminesulphonate end-point, and/or by impeding visual observation of the completion of the stannous chloride reduction stage[1]. Moderate amounts of chromium do not interfere.

Up to approximately 0.5 mg each of copper, vanadium, and molybdenum[3], and up to approximately 2 mg of tungsten[5] do not cause significant error in the iron result. Interference from more than 0.5 mg of copper and molybdenum, and from platinum is eliminated by separating iron from these elements, and from calcium, magnesium, manganese, zinc, nickel, cobalt, cadmium, and some tungsten by precipitation as the hydrous oxide with ammonium hydroxide from an ammonium chloride medium[5]. Interference from arsenic and antimony, and from large amounts of chromium can be avoided by volatilizing these elements as the bromides, and chromyl chloride from a hydrobromic-perchloric and a hydrochloric-perchloric acid medium, respectively. Iron is separated from large amounts of vanadium and tungsten, and from various other elements [e.g., chromium (VI), phosphate, aluminum, zinc, tin, and lead], including arsenic, antimony, molybdenum, platinum, and some uranium and gold by precipitating it as the hydrous oxide from a sodium hydroxide-hydrogen peroxide medium[4,5,9]. Interference from titanium (III) is avoided by oxidizing it to the tetravalent state with potassium chlorate (or with nitric or perchloric acids) during sample decomposition[1]. Interference from carbonaceous material is also avoided by this procedure.

Uranium and gold interfere in this method because they are not completely separated from iron by any of the separation procedures described. Zinc, aluminum, manganese, nickel, and cobalt do not interfere[7].

NOTE:

> For samples containing uranium, gold, vanadium, and moderate amounts of copper, molybdenum, tungsten, arsenic, and antimony, the Volumetric-Hydrogen Sulphide-Dichromate Method for total iron (p 287) is recommended.

Range

The method is suitable for samples containing more than approximately 0.5% of iron.

Reagents

Standard potassium dichromate solution, 0.1 N. Dissolve 9.8070 g of pulverized reagent (dried at 105°C for 1-2 hours) in water, and dilute to 2 litres (Note 1).

Stannous chloride solution, 5% w/v. Dissolve 12.5 g of stannous chloride dihydrate in 50 ml of hot, concentrated hydrochloric acid, and dilute to 250 ml with water. Add several pieces of tin metal, and store the solution in a dark bottle.

Ferrous ammonium sulphate solution, 0.1 N. Dissolve 3.9216 g of ferrous ammonium sulphate hexahydrate in 5% sulphuric acid, and dilute to 100 ml with the same solution.

Sodium diphenylaminesulphonate (oxidized) indicator tablets (0.001 g). If tablets are not available an oxidized solution of the indicator can be prepared as follows[10]:

> Dissolve 0.27 g of sodium diphenylaminesulphonate in 100 ml of water, add 10 ml of 50% sulphuric acid, cool, and dilute the solution to 300 ml with water. Slowly add 25 ml of 0.1 N potassium dichromate solution in small increments, followed by 8 ml of 0.1 N ferrous ammonium sulphate solution, then allow the resultant green mixture to stand for 3-4 days or until a portion of the supernatant solution yields no colour with a solution containing 100 ml of 5% sulphuric acid and 2 ml of 0.1 N potassium dichromate solution. Carefully siphon off the supernatant solution, add 300 ml of water and 15 ml of concentrated sulphuric acid, and siphon again after the precipitate has settled. Centrifuge, and wash the precipitate

with 5% sulphuric acid. Shake the washed precipitate with 100 ml of water, transfer the resulting suspension to a small brown glass bottle, and shake well before use.

Mercuric chloride solution, saturated.

Sodium hydroxide solutions, 10% and 20% w/v. Prepare fresh as required.

Hydrochloric acid wash solutions, 50%, 30%, 10% and 2% v/v.

Sodium hydroxide-sodium sulphate wash solution, 2% and 1% w/v, respectively.

Ammonium hydroxide wash solution, 2% v/v.

Sulphuric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Phosphoric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Water (oxygen-free). Freshly boiled and cooled water.

Standardization of potassium dichromate solution

Transfer 0.2000 g of high-purity iron metal to a 600-ml beaker, cover the beaker, add 20 ml of concentrated hydrochloric acid, and heat gently until decomposition is complete. Remove the cover, wash down the sides of the beaker with a small amount of 10% hydrochloric acid, and dilute the solution to approximately 30 ml with the same solution. Heat the solution to just below the boiling point then, while stirring, reduce the iron by adding 5% stannous chloride solution, by drops, until the yellow colour of the ferric chloride just disappears. Add 1-3 drops in excess (Note 2) and cool the solution to room temperature in a water-bath. Add 10 ml of saturated mercuric chloride solution, mix, and allow the solution to stand for approximately 5 minutes (Note 3). Dilute the solution to approximately 300 ml with cold, oxygen-free water, add 10 ml each of 50% oxygen-free sulphuric and phosphoric acids (Note 4) and one sodium diphenylamine-sulphonate indicator tablet (or 5 drops of indicator solution), and immediately titrate the resulting solution with standard potassium dichromate solution to a violet-blue end-point (Note 5). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure (Note 6). Determine the normality of the potassium dichromate solution, and calculate the iron equivalent (mg/ml) (1 ml of 0.1 N potassium dichromate solution = 5.585 mg of iron).

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Ores and mill products, and slags

(a) Tungsten content 2 mg or less, and vanadium, molybdenum, and copper contents 0.5 mg or less

Transfer 0.25-1 g of powdered sample, containing up to approximately 250 mg of iron, to a 250-ml beaker, and add 30 ml of concentrated hydrochloric acid and 0.1 g of potassium chlorate crystals. Cover the beaker, heat gently until the decomposition of the sample or acid-soluble material is complete, then remove the cover and boil the solution for several minutes to expel chlorine (Notes 7-9). Dilute the resulting solution to approximately 50 ml with warm water and, if necessary, filter it (Whatman No 541 paper) into a 600-ml beaker (Note 10). Transfer the residue quantitatively to the filter paper, and wash the paper and residue thoroughly with warm 2% hydrochloric acid until the yellow colour of ferric chloride is no longer visible. Wash the paper and residue 6-8 times with warm water, then evaporate the filtrate and washings to approximately 25 ml (Note 11).

Transfer the paper and residue (Note 12) to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at 750°C. Cool the crucible, and add 1 ml of 50% sulphuric acid and 3-5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid. Fuse the residue with 1-2 g of sodium carbonate (Note 13) or 2-3 g of potassium pyrosulphate, cool, and transfer the crucible and contents to a 250-ml beaker. Add 50 ml of water, cover the beaker, and add 5 ml of concentrated hydrochloric acid in small increments. If necessary, heat gently to dissolve the melt, and remove the crucible and cover after washing them thoroughly with hot water. Dilute the resulting solution to approximately 100 ml with water, and neutralize it approximately with concentrated ammonium hydroxide to precipitate the hydrous oxide of iron. Add 5 ml in excess and boil the solution for several minutes to coagulate the precipitate. Allow the precipitate to settle, then filter the solution (Whatman No. 541 paper) and wash the precipitate 6-8 times with hot 2% ammonium hydroxide. Discard the filtrate and washings (Note 14). Dissolve the precipitate, using approximately 20 ml of hot 30% hydrochloric acid, and wash the paper 6-8 times with hot 2% hydrochloric acid, then 2-3 times with hot water. Collect the resulting solution in the beaker in which the precipitation was carried out, and discard the paper. Add the solution to the initial filtrate and evaporate the combined solution to approximately 25 ml. Wash down the sides of the beaker with a small amount of 10% hydrochloric acid, and proceed with the reduction and subsequent titration of iron as described above.

(b) Molybdenum and/or copper contents more than 0.5 mg; tungsten content 2 mg or less; and vanadium content 0.5 mg or less

Following sample decomposition (Note 15), filtration of the solution (Note 16), and subsequent decomposition of the acid-insoluble residue by fusion with sodium carbonate or potassium pyrosulphate as described above, add the dilute hydrochloric acid solution of the melt to the initial filtrate, and evaporate the combined solution to approximately 10 ml (Note 17) to remove some of the excess hydrochloric acid. Dilute the solution to approximately 200 ml with hot water, neutralize it approximately with concentrated ammonium hydroxide, add 10 ml in excess, and proceed with the ammonium hydroxide separation of iron (Note 18) and the dissolution of the precipitate as described above. Add 15 ml of concentrated hydrochloric acid to the resulting solution, and evaporate it to approximately 25 ml. Wash down the sides of the beaker with a small amount of 10% hydrochloric acid, and proceed with the reduction and titration of iron.

(c) Vanadium content more than 0.5 mg and/or tungsten content more than 2 mg; copper content 0.5 mg or less

Following sample decomposition (Notes 15 and 19), filtration of the solution (Note 16), and treatment of the acid-insoluble residue as described in Procedure A(a), add the dilute hydrochloric acid solution of the melt to the initial filtrate, and evaporate the combined solution to approximately 10 ml to remove some of the excess hydrochloric acid. Dilute the solution to approximately 100 ml with water, and add 20% sodium hydroxide solution until the solution is almost neutral. Heat the solution to the boiling point and, while stirring, slowly pour it into a 600-ml beaker containing 100 ml of 10% sodium hydroxide solution and 2-3 ml of 30% hydrogen peroxide. Boil the resulting solution for several minutes, allow it to stand for approximately 15 minutes, then filter the solution (Whatman No. 541 paper) and wash both beakers, the paper, and the precipitate thoroughly with hot 2% sodium hydroxide-1% sodium sulphate solution. Discard the filtrate and washings.

Dissolve the precipitate, using approximately 20 ml of hot 30% hydrochloric acid, and wash the paper 6-8 times with 2% hydrochloric acid, then 2-3 times with hot water (Note 20). Collect the solution in the beaker in which the precipitation was carried out, and discard the paper. Wash the original beaker 3 times with a small amount of 10% hydrochloric acid and add the washings to the solution containing the iron. Add 15 ml of concentrated hydrochloric acid to the resulting solution and evaporate it to approximately 25 ml. Wash down the sides of the beaker with a small amount of 10% hydrochloric acid, and proceed with the reduction and titration of iron.

(d) Vanadium, molybdenum, and copper contents more than 0.5 mg, and tungsten content more than 2 mg

Following the separation of iron from vanadium, tungsten, and molybdenum by precipitation as the hydrous oxide, and the dissolution of the precipitate as described in Procedure A(c), evaporate the resulting solution to approximately 10 ml, and proceed with the ammonium hydroxide separation and subsequent determination of iron as described in Procedure A(b).

Alternatively, iron can first be separated from copper and molybdenum by precipitation as the hydrous oxide as described in Procedure A(b), followed by dissolution of the precipitate and evaporation of the resulting solution to approximately 10 ml. Iron can subsequently be separated from vanadium and tungsten and determined as described in Procedure A(c).

B - Acid-soluble silicate rocks and minerals, carbonate rocks, clay, and shale

Transfer 0.5-1 g of powdered sample, containing up to approximately 150 mg of iron, to a 100-ml platinum dish (Note 21), moisten with several ml of water (Note 22), and add 15 ml of concentrated hydrofluoric acid. Allow the mixture to digest at room temperature for approximately 30 minutes, then add 10 ml each of concentrated hydrochloric and perchloric acids, and evaporate the solution to fumes of perchloric acid. Cool, add 10 ml each of water and concentrated hydrofluoric and hydrochloric acids, evaporate the solution to fumes again and, if necessary, repeat the addition of hydrofluoric and hydrochloric acids and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water and evaporate the solution to fumes. Repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid, then evaporate the solution to 3-4 ml. Cool, add approximately 10 ml of water and 10 ml of concentrated hydrochloric acid (Note 17), and heat gently until the solution becomes clear (Note 23). Transfer the resulting solution to a 600-ml beaker, dilute to approximately 200 ml with water, and proceed with the ammonium hydroxide separation of iron (Note 24), the dissolution of the precipitate (Note 25), and the subsequent determination of iron as described in Procedure A(b).

C - Refractory silicate rocks and minerals

Transfer 0.5-1 g of powdered sample, containing up to approximately 150 mg of iron, to a 30-ml platinum crucible, and ignite in a muffle furnace at 800-900°C for approximately 30 minutes (Note 26). Cool the crucible, add a five-fold weight excess of sodium carbonate, mix, and cover the mixture with 0.5-1 g of sodium carbonate. Cover the crucible with a platinum cover, heat at a low temperature for 5-10 minutes, then fuse the mixture at 900-1000°C for approximately 30 minutes (Note 13). Remove the cover, swirl the crucible to distribute the melt in a thin layer around the inner walls, and allow the crucible and contents to cool. Transfer the crucible and cover to a 400-ml (covered) Teflon beaker containing approximately 40 ml of water, and add 30 ml of concentrated perchloric acid in small portions. When dissolution of the melt is complete, remove the crucible and cover after washing them thoroughly with hot water, add 10 ml of concentrated hydrofluoric acid, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, evaporate the solution to fumes again, then repeat the washing and evaporation steps two more times to ensure the complete removal of hydrofluoric acid. Evaporate the solution to approximately 5 ml or until the sodium salts begin to crystallize, cool, add approximately 25 ml of water and 10 ml of concentrated hydrochloric acid, and heat gently to dissolve the salts. Transfer the resulting solution to a 600-ml beaker, dilute to approximately 200 ml with water, and proceed with the ammonium hydroxide separation of iron (Note 14), the dissolution of the precipitate (Note 25), and the subsequent determination of iron as described in Procedure A(b).

Notes

1. If pure dry potassium dichromate is employed, standardization of the solution is not necessary.

2. The excess of stannous chloride solution should not exceed 0.2 ml. A larger excess may result in the formation of finely-divided free mercury (indicated by a gray or black precipitate) according to the reaction

$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg\downarrow ;$$

this ruins the determination because it reacts with the titrant. A large excess may also result in the formation of excessive amounts of mercurous chloride, which also reacts, to some extent, with the titrant[5,10]. If enough stannous chloride solution has been added, a slight silky precipitate of mercurous chloride is obtained[5].

3. If the time interval, after the addition of mercuric chloride solution, is less than 5 minutes, high results may be obtained because of incomplete oxidation of the excess stannous chloride; a longer time interval may cause low results[1].

4. Because the redox potential of the indicator is less than that of the ferrous-ferric couple near the end-point, the addition of phosphoric acid is necessary. This acid lowers the oxidation potential of the ferrous-ferric system by forming a colourless complex with the ferric ion; this also makes the end-point easier to detect[10].

5. Near the end-point the solution will become green, and then blue-green, or grayish-blue in the presence of large amounts of iron. At this point, the dichromate solution should be added carefully, by drops, until the violet-blue end-point is reached. Over-titration can readily be avoided by titrating the solution first, without phosphoric acid, to the dark green colour (approximately 1.5% before the end-point), and then adding the phosphoric acid and titrating to the end-point[10]. The titration should be completed as quickly as possible because of the possible reaction

$$Hg_2Cl_2 + 2FeCl_3 \rightarrow 2HgCl_2 + 2FeCl_2$$

between mercurous chloride and iron (III)[11].

A 0.2000-g portion of iron metal requires 35.81 ml of 0.1 N potassium dichromate solution.

6. In the absence of iron, the sodium diphenylaminesulphonate indicator does not react with the potassium dichromate solution. In the presence of small amounts of iron, the indicator response is slow[2]. Therefore, to avoid over-titration of the blank solution, because of the slowness of the indicator change, the addition of 1 ml of 0.1 N ferrous ammonium sulphate solution, just prior to titration with potassium dichromate solution, is recommended to promote indicator response. The ferrous ammonium sulphate solution employed should be standardized against 0.1 N potassium dichromate solution as follows[12]:

Add 10 ml each of 50% oxygen-free sulphuric and phosphoric acids to a 600-ml beaker, dilute to 300 ml with water, and add 1 ml of 0.1 N ferrous ammonium sulphate solution and one sodium diphenylaminesulphonate indicator tablet. Carefully titrate to the first appearance of the deep violet colour, then add 25 ml of the iron (II) solution and titrate to the end-point. Calculate the dichromate equivalent of the ferrous ammonium sulphate solution from the volume required to oxidize the iron in the 25-ml aliquot.

The volume of 0.1 N potassium dichromate solution required by the blank solution (which includes the indicator blank) is subsequently determined by subtracting the volume (calculated) of dichromate solution equivalent to 1 ml of 0.1 N ferrous ammonium sulphate solution.

An alternative method of correcting for the blank involves the addition of 1 ml of 0.1 N ferrous ammonium sulphate solution to both the blank and the reduced iron solution, just prior to titration. The result obtained for the iron solution is then corrected by subtracting that obtained for the blank solution. This method precludes the necessity for standardizing the ferrous ammonium sulphate solution.

7. Unless iron is to be determined by Procedures A(c) and (d), arsenic and antimony, if present, should be removed at this stage by volatilization as the bromides, as follows:

Add 10 ml each of concentrated hydrobromic and perchloric acids and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the beaker with water, and add a further 10 ml-portion of hydrobromic acid. Evaporate the solution to 3-4 ml, then add 30 ml of concentrated hydrochloric acid, heat to dissolve the salts, and proceed as described.

Tin is also volatilized as the bromide by the above procedure.

8. Decomposition with hydrochloric acid alone is generally satisfactory for most types of iron ore, sinters, blast-furnace, and basic slags. Basic slags and blast-furnace slag samples should first be boiled with water, followed by slow addition of the hydrochloric acid to prevent coagulation of the sample into globules that are resistant to attack. The decomposition of less soluble ore and mill product materials can be facilitated by the addition of concentrated hydrofluoric acid, using a Teflon beaker for decomposition, followed by evaporation of the sample solution to fumes of perchloric acid or to fumes of sulphur trioxide to remove the excess hydrofluoric acid[1].

Other recommended methods of decomposition for certain ores and mill products, and slags are as follows[1,13]:

(a) Iron oxides, including red and brown hematites, magnetic iron ore, spathose iron ore, roasted pyrites, and iron ore briquettes can be decomposed by heating at 80-90°C with hydrochloric acid and several drops of 5% stannous chloride solution. More stannous chloride solution, which greatly facilitates sample decomposition, may be required to obtain complete decomposition of the sample, but the addition of an excess, sufficient to completely de-colourize the solution, should be avoided. This necessitates re-oxidation of the iron with hydrogen peroxide, followed by vigorous boiling to remove excess hydrogen peroxide, prior to the reduction and subsequent titration of the iron. If a coloured residue remains, it should be removed by filtration, ignited in a platinum crucible, and treated as described in the subsequent procedure. Following dissolution of the resultant hydrous iron oxide precipitate (Note 14) with dilute hydrochloric acid, the resulting solution should be added to the initial filtrate.

Sulphide ores containing organic material should be roasted in a porcelain crucible over an open flame for approximately 30 minutes until oxidized, then dissolved as described above.

(b) Refractory iron ores containing an appreciable amount of silica can be decomposed by fusion in a platinum crucible with a mixture of sodium and potassium carbonates (Note 13). Oxide ores containing small amounts of silica can be decomposed by fusion with potassium pyrosulphate in a vitreosil crucible. The melts obtained should subsequently be dissolved in dilute hydrochloric acid, and iron should be precipitated as the hydrous oxide as described in Procedure A(b), if necessary, to remove any platinum that may have been introduced into the melt during fusion of the sample in a platinum crucible. If sample decomposition following fusion with potassium pyrosulphate is incomplete, it may be necessary (Note 12) to treat the insoluble residue with sulphuric and hydrofluoric acids, followed by fusion with sodium carbonate, and separation of iron from platinum as the hydrous oxide, as described in the subsequent procedure.

(c) Acid slags are decomposed best by treatment with sulphuric, nitric, and hydrofluoric acids in a Teflon beaker, followed by evaporation of the solution to fumes of sulphur trioxide to remove excess nitric and hydrofluoric acids.

(d) Titanium ores and mill products can be satisfactorily decomposed by fusion with potassium pyrosulphate in a vitreosil crucible if all of the iron minerals are soluble. If insoluble iron silicates are present the sample can be decomposed in a Teflon beaker with hydrofluoric and sulphuric acids, followed by evaporation of the solution to fumes of sulphur trioxide to remove excess hydrofluoric acid.

(e) Manganese ores and mill products can be decomposed by treatment with hydrochloric and sulphurous acids, or by treatment with hydrochloric, nitric, and sulphuric acids, followed by evaporation of the solution to fumes of sulphur trioxide to remove excess nitric acid.

(f) Chromium ores and mill products can be decomposed with hydrochloric, nitric, and perchloric acids, followed by evaporation of the solution to fumes of perchloric acid. Chromium can subsequently be removed by volatilization as chromyl chloride, by the repeated addition of small increments of concentrated hydrochloric acid, and subsequent evaporation of the solution to fumes of perchloric acid.

If any of the above decomposition procedures are employed, proceed with the determination of iron as described in Procedures A(a) to (d), depending on the amount of vanadium, molybdenum, tungsten and/or copper present. If the sample contains titanium, care must be taken that it is oxidized to the tetravalent state, either during or after sample decomposition (Note 9). Antimony and arsenic, if present, must be removed by volatilization as the bromides as described in Note 7, prior to the reduction and titration of the iron. If the sample solution contains an appreciable amount of potassium salts, resulting from fusions with potassium pyrosulphate or a mixture of sodium and potassium carbonates, antimony and arsenic should be removed by volatilization from a hydrobromic-sulphuric acid medium. Sufficient concentrated hydrochloric acid (i.e., 20-25 ml) must be present in the sample solution, prior to the reduction step, to provide for the reduction of iron.

9. The addition of potassium chlorate crystals to oxidize titanium is not necessary if nitric or perchloric acids are employed for sample decomposition (Note 8).

10. If no acid-insoluble residue is present, proceed as described with the reduction and subsequent titration of total iron.

11. If only hydrochloric acid-soluble iron is required, discard the residue, and proceed with the reduction and titration of iron.

12. If only a small amount of residue is present, and it is perfectly white, the subsequent treatment of the residue may be omitted without causing significant error in the iron result[3].

13. Oxidizing conditions must be maintained during fusions with sodium carbonate, or else iron and other easily reducible elements (e.g., lead and zinc) will alloy with the platinum crucible. If a flame is employed for fusion, the mixture should be heated gradually to avoid loss by spattering, the flame should not be allowed to envelop the crucible completely, and the bottom of the crucible should never be allowed to come into contact with the blue cone of the burner flame. Flame fusions generally result in some loss of iron from the sample material to the platinum crucible. The presence of an oxidizing atmosphere during fusion can be ensured by employing a muffle furnace, started cold, or at a temperature below 500°C, followed by gradual heating to the desired temperature (i.e., 900-1000°C).

14. This separation procedure is necessary to eliminate any platinum that may have been introduced into the melt during fusion of the residue in the platinum crucible[5,6].

15. Samples containing more than approximately 150 mg of iron cannot be conveniently handled by this method because of the bulkiness of the iron (III) hydrous oxide precipitate.

16. If only acid-soluble iron is required, discard the residue, evaporate the filtrate to approximately 10 ml, and proceed with the separation and subsequent titration of iron.

17. Approximately 10 ml of concentrated hydrochloric acid should be present at this stage to provide sufficient (2-3% w/v) ammonium chloride (formed during neutralization of the solution with ammonium hydroxide) to maintain calcium, magnesium, and manganese in solution during the subsequent ammonium hydroxide separation of iron (1 ml of concentrated hydrochloric acid = 0.625 g of ammonium chloride).

18. If the sample contains an appreciable amount of molybdenum and/or copper, re-precipitation of the hydrous oxide of iron is recommended to ensure the complete removal of any of these elements that may have been occluded or adsorbed by the precipitate.

19. Alternatively, samples of iron ore can be decomposed by fusion in an Alundum crucible with a ten-fold weight excess of a 30% sodium carbonate-70% sodium peroxide mixture, and the iron can be separated directly from vanadium, tungsten, and molybdenum by filtration of an aqueous solution of the melt[2]. If this method is employed proceed as follows:

Transfer the crucible and cooled melt to a 250-ml beaker, add approximately 100 ml of water, and boil gently to disintegrate the melt. Remove the crucible after washing it thoroughly with hot water, and filter, wash, and dissolve the precipitate as described. Wash the crucible with hot 50% hydrochloric acid, add the washings to the solution containing the iron, then proceed as described. If re-precipitation of iron is necessary (Note 20), evaporate the solution to 10 ml, and precipitate with 10% sodium hydroxide solution in the presence of hydrogen peroxide as described.

20. If the sample contains an appreciable amount of vanadium, tungsten, and/or molybdenum, re-precipitation of the hydrous oxide of iron is recommended to ensure the complete removal of any of these elements that may have been occluded or adsorbed by the precipitate.

21. Teflon beakers can also be employed for sample decomposition, but the point at which decomposition is complete is more difficult to detect than in a platinum dish because of the white colour of the beaker. If complete decomposition can be readily obtained by the subsequent treatment with acids, and if the sample does not contain platinum, more than approximately 2 mg of tungsten, or more than 0.5 mg of copper, molybdenum, and/or vanadium, the use of a Teflon beaker is advantageous because the subsequent ammonium hydroxide separation of iron (Note 24) is not necessary. If a Teflon beaker is employed under the above conditions, add 10 ml of water and 20 ml of concentrated hydrochloric acid after the initial evaporation of the solution to 3-4 ml. Heat until the solution becomes clear, transfer it to a 600-ml beaker, evaporate the solution to approximately 25 ml, and proceed directly with the reduction and subsequent titration of iron.

22. To avoid loss of sample resulting from the rapid reaction between carbonates and acid, if the sample is a carbonate rock, moisten the sample with approximately 10 ml of water, cover the beaker, and add 10 ml of concentrated hydrochloric acid in small portions. When the decomposition of the carbonates is complete, add the recommended amounts of hydrofluoric and perchloric acids and proceed as described.

23. If complete decomposition of the sample could not be obtained by treatment with hydrofluoric, hydrochloric, and perchloric acids, and an appreciable amount of acid-insoluble material is present (Note 12), it should be removed by filtration, ignited in a platinum crucible, and treated as described in Procedure A(a). Following dissolution of the sodium carbonate or potassium pyrosulphate melt in dilute hydrochloric acid, add the resulting solution to the initial filtrate, then proceed as described. Alternatively, it may be advantageous to determine iron by the method described in Procedure C.

24. This separation procedure is necessary to eliminate any platinum that may have been introduced into the solution during sample decomposition in the platinum dish[5]. Copper and molybdenum are also removed by this procedure. However, with the exception of copper- and molybdenum-bearing minerals, the sample materials mentioned usually do not contain these elements in sufficient amounts to cause significant error in the iron result.

25. If the sample contains more than approximately 0.5 mg of vanadium and/or 2 mg of tungsten, evaporate the solution obtained after the dissolution of the hydrous iron oxide precipitate to approximately 10 ml, dilute to 100 ml with water, and proceed with the sodium hydroxide-hydrogen peroxide separation and the subsequent determination of iron as described in Procedure A(c). With the exception of tungsten-bearing minerals, the sample materials mentioned usually do not contain tungsten or vanadium in sufficient amounts to cause significant error in the iron result.

26. Ignition of the sample oxidizes any reducing substances (e.g., carbonaceous material and pyrite) that could attack the platinum crucible during the subsequent fusion procedure.

Calculations

Normality of potassium dichromate solution (N_{KD})

$$= \frac{\text{Weight of iron (g)}}{0.05585 \times (V-v)}$$

where:

V = volume (ml) of potassium dichromate solution required by the iron.

v = volume (ml) of potassium dichromate solution required by the blank.

Iron equivalent (mg/ml) of the potassium dichromate solution (Fe_{EQ})

$$= N_{KD} \times 55.85$$

OR

$$= \frac{\text{Weight of iron (mg)}}{V-v}$$

where:

V and v are as described above

$$\% \text{ Fe} = \frac{(V_S - V_B) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium dichromate solution required by the sample.

V_B = volume (ml) of potassium dichromate solution required by the blank.

$\% \ Fe_2O_3 = 1.430 \times \% \ Fe$

$\% \ FeO = 1.287 \times \% \ Fe$

$\% \ Fe_3O_4 = 1.382 \times \% \ Fe$

Other applications

With suitable modifications in the decomposition and separation procedures, the methods described in Procedures A(a) to A(d) can be employed to determine iron in silica-base and chrome-magnesite refractories, and ferrous alloys[1]. The method described in Procedure B is applicable to firebrick, cement, and glass, and that in Procedure C is applicable to bauxite and magnesite.

References

1. Methods of Analysis Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association, "Determination of Iron in Ores, Slags, and Refractories", J. Iron and Steel Inst., 171, 392 (1952).
2. Technical Committee 102 - Iron Ores, "Determination of Total Iron Content", International Organization for Standardization, Document 103E, March (1970).
3. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E277-69, pp 758-761 (1971).
4. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Dept. of Energy, Mines and Resources, Mines Branch, Ottawa, Mines Branch Monograph 866, Part III, Method No. Fe-3, April (1958).
5. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis" 2nd ed., John Wiley and Sons, Inc., New York, pp 384-397 (1953).
6. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 2, pp 273-275, 293-294 (1962).
7. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 539, 542-544 (1962).
8. Idem., Ind. Eng. Chem., 17, 314 (1925).
9. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 81-85 (1938).
10. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, pp 170-178 (1957).
11. Idem, ibid., pp 10-11 (1957).

12. Idem, ibid., 181 (1957).

13. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 530-531, 546-547, 1114 (1962).

DETERMINATION OF TOTAL IRON IN ORES AND MILL PRODUCTS, AND SLAGS BY TITRATION WITH POTASSIUM DICHROMATE AFTER REDUCTION WITH HYDROGEN SULPHIDE

Principle

This method[1-3] is based on the reduction of iron to the divalent state with hydrogen sulphide in an approximately 0.36 M sulphuric acid medium. Iron is determined by titration of the resultant iron (II) with potassium dichromate, in an approximately 0.5 M sulphuric-0.2 M phosphoric acid medium, in the presence of sodium diphenylaminesulphonate as internal indicator.

The corresponding reactions for these processes are:

$$Fe_2(SO_4)_3 + H_2S \rightarrow 2FeSO_4 + H_2SO_4 + S\downarrow$$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Outline

The sample is decomposed with hydrochloric and nitric acids (or by treatment with other suitable acids, or by fusion with a suitable flux, depending on the type of sample material). The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate or potassium pyrosulphate, the melt is dissolved in dilute hydrochloric acid, and the solution is added to the initial filtrate. Nitric acid is removed by evaporation of the combined solution with sulphuric acid, and iron is ultimately reduced with hydrogen sulphide. After removal of the insoluble sulphides by filtration, the iron in the resulting filtrate is ultimately titrated with potassium dichromate solution.

Discussion of interferences

None of the elements that interfere in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 275) because of their reduction and subsequent oxidation by potassium dichromate (i.e., arsenic, antimony, platinum, gold, molybdenum, tungsten, and uranium), including copper which interferes in the above method by accelerating the air-oxidation of iron (II), interfere in the titration of iron with potassium dichromate after its reduction to the divalent state with hydrogen sulphide[1,3,4]. Uranium is not reduced with hydrogen sulphide, and arsenic, antimony, platinum, gold, molybdenum, copper, and various other elements (e.g., mercury, bismuth, cadmium, lead, tin, selenium, silver, and palladium) are precipitated as the sulphides during the reduction step, and are separated from iron by filtration. Tungsten (VI) is hydrolyzed, to a large extent, in the dilute sulphuric acid medium employed for reduction, and is subsequently removed with the sulphide precipitate. Residual tungsten (VI) remaining in the filtrate does not interfere in the determination of iron. Vanadium does not interfere because it is reduced to the tetravalent state.

Because of its intense colour in solution, chromium (III), if present in large amounts, may interfere by masking the violet-blue sodium diphenylaminesulphonate end-point. Interference from large amounts of chromium can be avoided by volatilizing it as chromyl chloride from a hydrochloric-perchloric acid medium. Moderate amounts of chromium do not interfere.

Interference from titanium (III), initially present in the sample, is avoided by oxidizing it to the tetravalent state with nitric acid during sample decomposition[1]; titanium (IV) is not reduced to the trivalent state with hydrogen sulphide. Interference from carbonaceous material is also avoided by this procedure.

Range

The method is suitable for samples containing more than approximately 0.5% of iron, but samples containing lower concentrations can also be analyzed if more dilute (e.g., 0.02 N) potassium dichromate solution is employed as titrant[1].

Reagents

Standard potassium dichromate solution, 0.1 N. Prepare as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 276).

Ferrous ammonium sulphate solution, 0.1 N. Prepare as described in the above method for iron.

Sodium diphenylaminesulphonate (oxidized) indicator tablets (0.001 g) or oxidized solution. Prepare the solution as described in the above method for iron.

Potassium permanganate solution, 0.5% w/v.

Bromine water. Water saturated with bromine.

Nitric acid-bromine water solution, 10% and 5% v/v, respectively.

Sulphuric acid, 50% v/v.

Phosphoric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide wash solution. 2% sulphuric acid saturated with hydrogen sulphide.

Hydrochloric acid wash solution, 2% v/v.

Water (oxygen-free). Freshly boiled and cooled water.

Standardization of potassium dichromate solution

Standardize the solution against pure iron as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure. Determine the normality of the potassium dichromate solution, and calculate the iron equivalent (mg/ml) (1 ml of 0.1 N potassium dichromate solution = 5.585 mg of iron).

Alternatively, the potassium dichromate solution can be standardized against a sample of iron ore of known iron content, or against pure iron metal (0.2000 g), after carrying these materials through the described procedure, and the iron equivalent can be determined by direct calculation.

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.25-1 g of powdered sample, containing up to approximately 250 mg of iron, to a 250-ml beaker and add 25 ml of concentrated hydrochloric acid. Cover the beaker, and heat gently until the decomposition of the sample or acid-soluble material is complete (Note 1). Add 5 ml of concentrated nitric acid, heat gently for 15 minutes (Note 2), then remove the cover, and dilute the solution to approximately 50 ml with warm water. If necessary, filter the solution (Whatman No. 541 paper) into a 600-ml beaker (Note 3), transfer the residue quantitatively to the filter paper, and wash the paper and residue thoroughly with warm 2% hydrochloric acid until the yellow colour of ferric chloride is no longer visible. Wash the paper and residue 6-8 times with warm water (Note 4), then evaporate the filtrate and washings to approximately 25 ml.

Transfer the paper and residue to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at 750°C. Cool the crucible, and add 1 ml of 50% sulphuric acid and 3-5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid. Fuse the residue with 1-2 g of sodium carbonate (Note 5) or 2-3 g of potassium pyrosulphate, cool, and transfer the crucible and contents to a 250-ml beaker. Add 25 ml of water, cover the beaker, and add 5 ml of concentrated hydrochloric acid in small increments. If necessary, heat gently to dissolve the melt, then remove the crucible after washing it thoroughly with hot water, and add the resulting solution to the initial filtrate.

Add 10 ml of 50% sulphuric acid to the combined solution and evaporate it to fumes of sulphur trioxide (Note 6). Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool, dilute to approximately 100 ml with water and heat the solution to the boiling point. Add 0.5% potassium permanganate solution, by drops, until the solution is just pink, then add 0.5 ml in excess (Note 7). Dilute the resulting solution to approximately 250 ml with water, boil it for several minutes, remove the beaker from the hot-plate, and pass hydrogen sulphide through the solution for approximately 15 minutes. Digest the solution at approximately 60°C for 15 minutes, filter it (Whatman No. 42 paper) into a 1-litre Erlenmeyer flask, and wash the beaker, paper, and precipitate 12-15 times with hydrogen sulphide wash solution (Notes 8 and 9). Discard the paper and precipitate, and add 10 ml of 50% sulphuric acid to the filtrate. Add 4 or 5 glass beads to prevent bumping, and boil the solution for 10-20 minutes to expel hydrogen sulphide (Note 10). Cover the flask with a small watch glass and cool the solution to approximately 20°C in an ice-bath. If necessary, dilute the resulting solution to approximately 350 ml with oxygen-free water, add 10 ml of 50% oxygen-free phosphoric acid and one sodium diphenylaminesulphonate indicator tablet (or 5 drops of indicator solution), and immediately proceed with the titration of iron with 0.1 N potassium dichromate solution (Note 11), as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277). Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Notes

1. If only hydrochloric acid-soluble iron is required, omit the addition of nitric acid, filter the solution, and wash the paper and residue as described in the subsequent procedure. Discard the residue. Add 10 ml of 50% sulphuric acid to the filtrate, evaporate the solution to fumes of sulphur trioxide, then proceed as described with the hydrogen sulphide reduction and subsequent titration of iron.

2. Decomposition with hydrochloric and nitric acids is generally satisfactory for most types of iron ore, sinters, blast-furnace, and basic slags. Basic slags and blast-furnace slag samples should first be boiled with water, followed by slow addition of the hydrochloric acid to prevent coagulation of the sample into globules that are resistant to attack. The decomposition of less soluble ore and mill product materials can be facilitated by the addition of concentrated hydrofluoric and sulphuric acids, using a Teflon beaker for decomposition, followed by evaporation of the sample solution to fumes of sulphur trioxide to remove excess hydrofluoric acid[1].

Recommended methods of decomposition for certain ores and mill products, and slags are described in Note 8 (p 281) of the Volumetric-Stannous Chloride-Dichromate Method for total iron. If any of these decomposition procedures are employed and sulphuric acid was not used during sample decomposition, approximately 10 ml of 50% sulphuric acid must be added to the combined solution obtained after sample decomposition and treatment, if necessary (Note 4), of the residue. The solution must subsequently be evaporated to fumes of sulphur trioxide, before the hydrogen sulphide reduction step, to remove other acids that were employed for decomposition. It is not necessary to remove any platinum that may have been introduced into the solution because of sample decomposition in platinum dishes or crucibles. Platinum is precipitated as the sulphide during the hydrogen sulphide reduction step and subsequently separated from iron by filtration.

3. If no acid-insoluble residue is present, add 10 ml of 50% sulphuric acid, evaporate the solution to fumes of sulphur trioxide, and proceed as described with the reduction and titration of iron.

4. If only a small amount of residue is present, and it is perfectly white, the subsequent treatment of the residue may be omitted without causing significant error in the iron result[3].

5. Oxidizing conditions must be maintained during fusions with sodium carbonate, or else iron and other easily reducible elements (e.g., lead and zinc) will alloy with the platinum crucible. If a flame is employed for fusion, the mixture should be heated gradually to avoid loss by spattering, the flame should not be allowed to envelop the crucible completely, and the bottom of the crucible should never be allowed to come into contact with the blue cone of the burner flame. Flame fusions generally result in some loss of iron from the sample material to the platinum crucible. The presence of an oxidizing atmosphere during fusion can be ensured by employing a muffle furnace, started cold, or at a temperature below 500°C, followed by gradual heating to the desired temperature (i.e., 900-1000°C).

6. If the sample contains an appreciable amount of calcium, prolonged fuming with sulphuric acid may result in the formation of salts that are difficult to re-dissolve. In this case, allow the solution to fume just long enough to expel the hydrochloric and nitric acids, then cool the solution, wash down the sides of the beaker with water, and evaporate to light fumes of sulphur trioxide again[3].

7. The addition of potassium permanganate solution is necessary to ensure the complete oxidation of carbonaceous material and elements that could be present in the sample solution in their reduced forms (e.g., arsenic, antimony, titanium, tungsten, molybdenum, and vanadium), particularly if an oxidizing form (i.e., nitric and/or perchloric acid) of decomposition was not employed (Notes 1 and 2)[1].

8. To avoid possible loss of iron by adsorption or occlusion if the amount of precipitate obtained is large, the sulphides should be re-precipitated as follows:

Dissolve the precipitate, using 10% nitric acid-5% bromine water solution, and wash the paper thoroughly with hot water. Collect the solution in the beaker in which the precipitate was carried out, and discard the paper. Add 10 ml of 50% sulphuric acid to the resulting solution, evaporate it to fumes of sulphur trioxide twice to ensure the complete removal of nitric acid, and re-precipitate, filter, and wash the sulphide precipitate as described. Add the filtrate to the initial filtrate and proceed as described[1].

The resultant increase in volume of the sample solution does not affect the subsequent titration of iron.

9. Because some reduction of molybdenum occurs during the hydrogen sulphide separation, precipitation of this element may not be complete if an appreciable amount is present. Any molybdenum remaining in the filtrate may be removed as follows:

Boil the filtrate for 10-20 minutes (Note 10) to expel hydrogen sulphide, and add 5 ml of 0.5% potassium permanganate solution to oxidize the residual molybdenum. Repeat the hydrogen sulphide treatment, filter, and wash any further molybdenum sulphide obtained as described, then proceed as described[1].

The resultant increase in volume of the sample solution does not affect the subsequent titration of iron.

10. Usually a 10-minute boiling period is sufficient to expel the excess hydrogen sulphide, but its absence should be confirmed during the boiling stage by testing the vapour with lead acetate paper[1,2].

11. Samples containing less than approximately 0.5% of iron can be analyzed at this stage by employing more dilute (e.g., 0.02 N) potassium dichromate solution for the titration. However, ferrous ammonium sulphate solution of the same normality should be employed for the determination of the reagent blank, as described in Note 6 (p 280) of the Volumetric-Stannous Chloride-Dichromate Method for total iron (1 ml of 0.02 N potassium dichromate solution = 1.117 mg of iron).

Calculations

$$\% \text{ Fe} = \frac{(V_S - V_B) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium dichromate solution required by the sample.

V_B = volume (ml) of potassium dichromate solution required by the blank.

Fe_{EQ} = iron equivalent (mg/ml) of the potassium dichromate solution.

$\% Fe_2O_3 = 1.430 \times \% Fe$

$\% FeO = 1.287 \times \% Fe$

$\% Fe_3O_4 = 1.382 \times \% Fe$

Other applications

With suitable modifications in the decomposition procedure, this method can be employed to determine iron in silica-base and chrome-magnesite refractories, and ferrous alloys[1].

References

1. Methods of Analysis Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association, "Determination of Iron in Ores, Slags, and Refractories", J. Iron and Steel Inst., 171, 392 (1952).

2. Technical Committee 102 - Iron Ores, "Determination of Total Iron Content", International Organization for Standardization, Document 103E, March (1970).

3. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E246-68, pp 741-744 (1971).

4. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, 539 (1962).

DETERMINATION OF FERROUS IRON IN ACID-SOLUBLE SILICATE ROCKS AND MINERALS BY POTENTIOMETRIC TITRATION WITH CERIC SULPHATE AFTER ACID-DECOMPOSITION IN AN AIR-FREE ATMOSPHERE

Principle

This method[1] is a modification of that developed by Schafer[2], and involves the decomposition of the sample with hydrofluoric and sulphuric acids in an air-free atmosphere. Ferrous iron is determined by potentiometric titration with ceric sulphate in a 0.5 M sulphuric acid medium and a nitrogen atmosphere, according to the reaction

$$2FeSO_4 + Ce(SO_4)_2 \rightarrow Fe_2(SO_4)_3 + Ce(SO_4)_3.$$

Outline

The sample is decomposed with hydrofluoric and sulphuric acids in a plastic apparatus and a nitrogen atmosphere, and the excess hydrofluoric acid is complexed with boric acid. The ferrous iron in the resulting solution is titrated with ceric sulphate solution.

Discussion of interferences

Elements that are present in the sample in lower oxidation states [e.g., vanadium (III), vanadium (IV), molybdenum (III), molybdenum (V), and probably chromium (III), titanium (III), copper (I), tungsten (III), and tungsten (V)], cause high results for ferrous iron because they either reduce any iron (III) that is released during sample decomposition, or because they are also oxidized by the ceric sulphate[2-5]. Vanadium (V) causes low results by oxidizing the ferrous iron that is released during sample decomposition[4]. Manganese (IV) may interfere in a similar manner[2]. Carbonaceous material (excluding graphite) causes high results for ferrous iron because it is partly oxidized by the titrant.

Pyrite, which is normally resistant to decomposition with hydrofluoric and sulphuric acids, causes high results in the presence of ferric iron, if present in appreciable amounts, because it is partly soluble in the presence of iron (III), and the sulphide sulphur is oxidized to sulphur trioxide at the expense of the ferric iron in the sample, according to the reaction

$$S + 3Fe_2O_3 \rightarrow SO_3\uparrow + 6FeO.$$

This reaction produces an amount of ferrous iron equivalent to 10.5 times the amount of the sulphide sulphur that was decomposed, in addition to that resulting from the partial decomposition of the pyrite itself. Soluble sulphides (e.g., pyrrhotite) that decompose and evolve hydrogen sulphide during sample decomposition also cause high results because the hydrogen sulphide reduces some of the ferric iron that is released during sample decomposition, according to the reaction

$$H_2S + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4 + S\downarrow.$$

The positive error caused by sulphides tends to become greater if the sample contains large amounts of either or both sulphide and iron (III) compounds. The amount of soluble sulphides normally present in silicate rocks does not cause significant error in the ferrous iron result because most of the hydrogen sulphide that is evolved is purged from the solution with nitrogen during sample decomposition[3,4].

Silicate rocks do not usually contain pyrite[3], or vanadium, copper, molybdenum, and tungsten in sufficient amounts to cause significant error in the ferrous iron result. The method is not applicable to sulphide minerals, or to vanadium-, copper-, molybdenum-, and tungsten-bearing minerals. Metallic iron, if introduced into the sample during the grinding process, causes high results for ferrous iron because it is converted to ferrous sulphate during the sample decomposition step.

Range

The method is suitable for samples containing more than approximately 0.2% of ferrous iron.

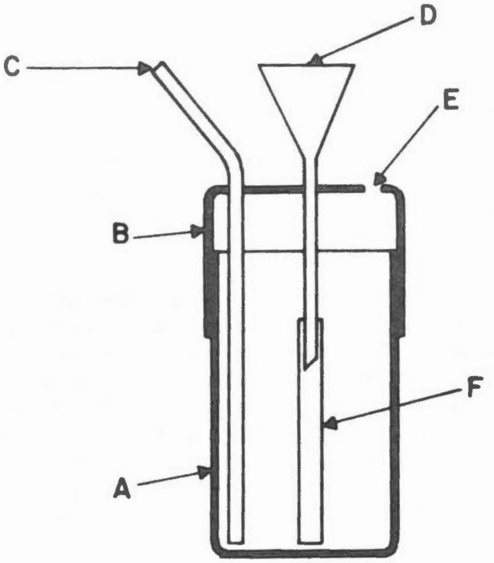

FIGURE 1. Apparatus for sample decomposition

A - Decomposition vessel (body of a 4-oz polyethylene bottle).
B - Cap (base of a 4-oz polyethylene bottle).
C - Nitrogen-inlet tube [Nalgene (polypropylene or polycarbonate) tubing -- inner and outer diameters approximately 2 mm and 5 mm, respectively] connected with rubber tubing to a nitrogen tank via a gas-control unit.
D - Nalgene funnel (approximately 10 ml capacity).
E - Nitrogen-outlet hole.
F - Nalgene tubing.

Apparatus

Apparatus for sample decomposition. Illustrated in Figure 1.

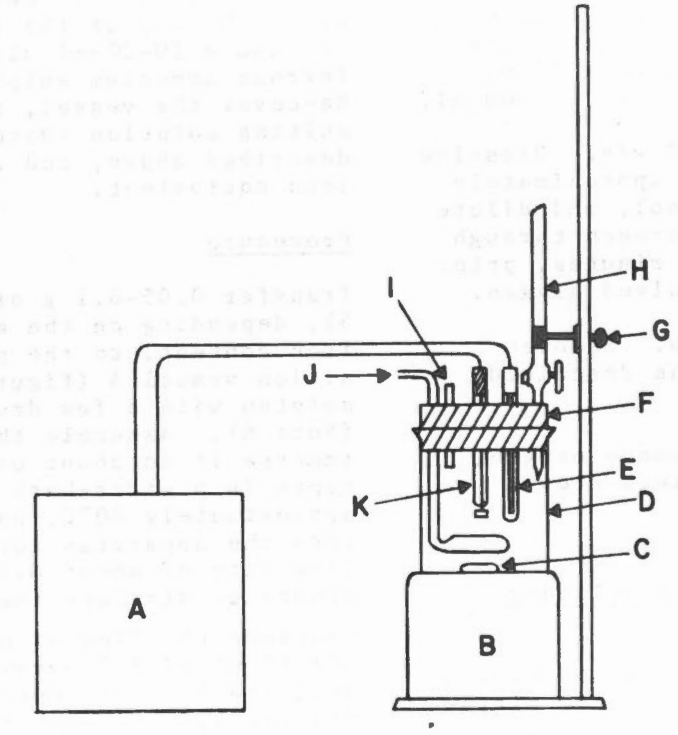

FIGURE 2. Apparatus for the potentiometric titration of ferrous iron

A - pH meter.
B - Magnetic stirrer.
C - Teflon-coated magnet.
D - Titration vessel (400-ml graduated beaker).
E - Calomel reference electrode.
F - Rubber cap.
G - Clamp.
H - Burette (25-ml).
I - Nitrogen-outlet tube.
J - Nitrogen-inlet gas-dispersion tube connected with rubber tubing to the nitrogen tank via a needle valve.
K - Platinum electrode.

Apparatus (continued)

Apparatus for the potentiometric titration of ferrous iron. Illustrated in Figure 2.

Reagents

Standard ceric sulphate solution, 0.01 N in 0.5 M sulphuric acid. Transfer 12.6516 g of ceric ammonium sulphate dihydrate [$Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$] or 10.9632 g of ceric ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$] to a dry 1-litre beaker, and add 55 ml of concentrated sulphuric acid. Mix for 2 minutes, then add water, in 25-ml portions, and stir for approximately 2 minutes after each addition until the salt is completely dissolved. Cool the resulting solution to room temperature and transfer it to a 2-litre volumetric flask. Dilute the solution to approximately 1980 ml with water, mix, cool to room temperature again, and dilute to volume with water.

Standard sodium oxalate solution, 0.01 N. Dissolve 0.1676 g of pure reagent (dried at 105°C for 1-2 hours) in water and dilute to 250 ml. Prepare fresh as required.

Standard ferrous ammonium sulphate solution, 0.01 N. Dissolve 0.3922 g of pure ferrous ammonium sulphate hexahydrate in oxygen-free water, add 5 ml of 50% oxygen-free sulphuric acid and dilute to 100 ml. Prepare fresh as required.

Manganous sulphate solution, 25% w/v. Dissolve 25 g of manganous sulphate monohydrate in approximately 75 ml of hot water, cool, and dilute to 100 ml.

Boric acid solution, 5% w/v. Dissolve 50 g of the reagent in approximately 800 ml of hot water, cool, and dilute to 1 litre. Bubble nitrogen through the solution for 10-15 minutes, prior to use, to remove dissolved oxygen.

Sulphuric acid, 50% v/v. Remove oxygen, prior to use, as described above.

Water (oxygen-free). Remove oxygen, prior to use, as described above.

Nitrogen (oxygen-free).

Standardization of ceric sulphate solution

Transfer a 10-20-ml aliquot of 0.01 N sodium oxalate solution to the titration vessel D (Figure 2), add 20 ml of 25% manganous sulphate solution (Note 1) and 14 ml of 50% sulphuric acid, and dilute the solution to approximately 250 ml with water. Remove the burette containing the ceric sulphate solution (Note 2) from the rubber cap F fitted with the electrodes, cover the titration vessel with the cap, and bubble nitrogen through the solution for about 5 minutes to remove dissolved air. Continue the flow of nitrogen, replace the magnetic stirrer B with an electric heating element, and heat the solution to approximately 60°C (Note 3). Replace the burette and magnetic stirrer, and titrate the solution potentiometrically with 0.01 N ceric sulphate solution. Determine the normality of the ceric sulphate solution, and calculate the iron equivalent (mg/ml) (1 ml of 0.01 N ceric solution = 0.5585 mg of iron).

Alternatively, the ceric sulphate solution may be standardized against pure ferrous ammonium sulphate as follows: Add 14 ml of 50% sulphuric acid to the titration vessel and dilute to approximately 230 ml with water. Cover the titration vessel with the rubber cap fitted with the electrodes, and bubble nitrogen through the solution for about 5 minutes. Then, while maintaining the flow of nitrogen, raise the rubber cap approximately one-quarter inch above the top of the titration vessel, and add a 10-20-ml aliquot of 0.01 N ferrous ammonium sulphate solution. Re-cover the vessel, titrate the resulting solution (Notes 3 and 4) as described above, and calculate the iron equivalent.

Procedure

Transfer 0.05-0.1 g of sample (Note 5), depending on the expected ferrous iron content, to the plastic decomposition vessel A (Figure 1), and moisten with a few drops of water (Note 6). Assemble the apparatus, immerse it to about one-third of its depth in a water-bath maintained at approximately 80°C, and pass nitrogen into the apparatus for 1 minute at a flow rate of about 0.5 litre per minute to displace the air.

Continue the flow of nitrogen, then add 14 ml of 50% oxygen-free sulphuric acid and 5 ml of concentrated hydrofluoric acid through the funnel, in succession, and swirl the apparatus - with both the nitrogen-inlet and acid-inlet tubes well below the surface of the solution - to disperse the sample. Repeat the swirling process several times during the decomposition procedure. When decomposition is complete (generally 45-90 minutes), add 40 ml of 5% oxygen-free boric acid solution through the funnel, and continue the flow of nitrogen for approximately 2 minutes to mix the solution. Stop the gas flow, remove the apparatus from the water-bath and, using oxygen-free water to wash the apparatus, transfer the sample solution, without delay, to the titration vessel containing 150 ml of water previously saturated with nitrogen for about 5 minutes. Dilute the resulting solution to 250 ml with oxygen-free water, cover the titration vessel with the rubber cap fitted with the electrodes, continue the flow of nitrogen, and proceed with the titration of ferrous iron as described above (Notes 7 and 8).

Notes

1. Manganous sulphate catalyzes the oxidation of sodium oxalate with ceric sulphate[6].

2. The burette is removed at this stage to prevent the ceric sulphate solution from expanding during the subsequent heating process.

3. Heating the solution to approximately 60°C, prior to titration, increases the rate of oxidation of sodium oxalate with ceric sulphate[6]. Heating is not required for the titration of ferrous iron with ceric sulphate solution.

4. Ferroin (1,10-phenanthroline ferrous sulphate) can be employed as internal indicator in the titration of ferrous iron with ceric sulphate solution[5], instead of titrating potentiometrically. Alternatively, potassium dichromate solution (e.g., 0.02 N) can also be employed, either for the potentiometric titration, or in the presence of sodium diphenylaminesulphonate as internal indicator[2,4,7] as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277) (1 ml of 0.02 N potassium dichromate solution = 1.117 mg of iron). If either of the above internal indicators is employed, the titration must be performed without delay to prevent air-oxidation of the ferrous iron, and the result obtained must be corrected for an indicator blank. If potassium dichromate solution (i.e., 0.02 N) and sodium diphenylaminesulphonate indicator are employed, ferrous ammonium sulphate solution of the same normality should be employed for the determination of the indicator blank, as described in Note 6 (p 280) of the Volumetric-Stannous Chloride-Dichromate Method for total iron, and 5 ml of concentrated phosphoric acid must be added to the solution prior to the titration of the iron (II). The addition of phosphoric acid is not necessary if potassium dichromate solution is employed for the potentiometric titration of the iron (II)[2,7].

Potassium permanganate solution is not recommended as a titrant for ferrous iron because positive error resulting from the oxidation of carbonaceous material is greater with potassium permanganate than with either ceric sulphate or potassium dichromate solution.

5. A sample that has been prepared by crushing, without grinding, in an agate (not iron or steel) mortar is preferable for the determination of ferrous iron. Fine grinding in air may result in considerable oxidation of ferrous iron in the sample because of the local heat generated during the grinding process. If a preliminary trial decomposition shows that only a small amount or no residue remains after the crushed sample has been gently boiled for approximately 20 minutes with concentrated hydrofluoric acid, this sample should be used directly for the ferrous iron determination. If a considerable amount of residue remains, grind a suitable weighed portion of the sample in an agate mortar, under absolute ethyl alcohol, just long enough to produce a powder that should subsequently yield only a small amount or no acid-insoluble residue. Allow the alcohol to evaporate spontaneously and, when the last trace has disappeared, transfer the powder from the mortar, and that adhering to the pestle to the plastic decomposition vessel, using a fine jet of water, and proceed as described. Because a considerable amount of water is absorbed by the sample during the above grinding process, the use of a weighed portion of a larger portion of sample, previously ground as described above, is not recommended. This necessitates the separate determination of both loosely- (hygroscopic moisture - H_2O^-) and firmly-bound (combined water - H_2O^+) water in order to correct the ferrous oxide result for the water that was absorbed during the grinding process[3].

6. It is not necessary to carry a reagent blank along with the samples because the blank correction is usually too small (approximately 0.01 ml of 0.01 N ceric sulphate solution) to cause significant error in the ferrous iron result.

7. Any acid-insoluble residue that is present in the solution after titration should be examined with a hand lens. Usually this residue will consist of white, or grayish-white

grains of quartz, which resist decomposition and which can be ignored. The presence of yellow grains of pyrite in the residue suggest that the ferrous iron result obtained is probably unreliable because of the possible presence of acid-decomposable sulphides (e.g., pyrrhotite) in the sample. If there are more than a few grains of un-decomposed red to black-coloured material in the residue, a second decomposition and titration should be carried out as follows[7]:

Carefully decant the supernatant solution from the titration beaker, and retain as much of the residue as possible in the beaker. Wash the beaker and residue once with water and decant the solution again. Using a fine jet of water, wash the residue into a small agate mortar, decant the water, and grind the residue until no gritty particles remain. Wash the mixture into the plastic decomposition vessel, repeat the decomposition and titration steps, and add the volume of titrant required to that required for the initial titration.

Any dark un-decomposed material that still remains after the above treatment is probably chromite, and will not decompose with further acid treatment. Because of the variable nature of chromite, it is not feasible to add a correction, based on the chromium content of the sample, to the ferrous iron result obtained[7].

8. If potassium dichromate solution (e.g., 0.02 N) and sodium diphenylaminesulphonate indicator (Note 4) have been employed for the titration of the ferrous iron, and if the total iron content of the sample was not previously determined by the Volumetric-Stannous Chloride-Dichromate Method for total iron (Procedure B p 279), the total iron, and subsequently the ferric iron content of the sample can be determined at this stage as follows[7]:

Add 25 ml of concentrated hydrochloric acid to the solution obtained after the titration of ferrous iron, or to the combined solution if the residue was re-treated as described in Note 7, and evaporate it to approximately 40 ml. If the resulting solution is not distinctly yellow or yellowish-green [because of the presence of chromium (III) from the initial titration], add sufficient dilute (approximately 2%) potassium permanganate solution, by drops, until the solution is yellow. Heat the solution to just below the boiling point, then, omitting the addition of the 50% sulphuric and phosphoric acids prior to the titration step, proceed with the stannous chloride reduction and subsequent determination of iron as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277).

Then,

$$\% \text{ Total iron} = \frac{(V_S - V_I) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = *volume (ml) of potassium dichromate solution required for the titration.*

V_I = *volume (ml) of potassium dichromate solution required for the indicator blank.*

Fe_{EQ} = *iron equivalent (mg/ml) of the potassium dichromate solution.*

% Ferric iron = % total iron − % ferrous iron.

% Total iron expressed as Fe_2O_3 = 1.430 x % total iron.

% Ferric iron expressed as Fe_2O_3 = 1.430 x % ferric iron.

If potassium dichromate solution (e.g., 0.02 N) has been employed for the potentiometric titration of ferrous iron, proceed as follows[7]:

Add 25 ml of concentrated hydrochloric acid to the solution, or to the combined solution obtained after the titration of ferrous iron, and evaporate it to approximately 40 ml. Heat the solution to just below the boiling point and, omitting the subsequent addition of mercuric chloride solution, reduce the iron with stannous chloride solution, as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277), and add 1-3 drops in excess. Dilute the solution to approximately 250 ml with oxygen-free water, cover the titration vessel with the rubber cap fitted with the electrodes, and carefully add potassium dichromate solution, by drops, to oxidize the excess stannous *chloride. [The end-point for the tin (II) oxidation should be indicated by a sudden increase in potential of about 50 millivolts in the neighborhood of a potential of approximately 300 millivolts.] Record the volume of titrant required to reach this first end-point, then continue with the potentiometric titration of iron until the end-point has been obtained.*

If the titration is not satisfactory, the solution can be evaporated to approximately 40 ml again, and the reduction and titration can be repeated.

Then,

$$\% \text{ Total iron} = \frac{(V_S - V_{Sn}) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S and Fe_{EQ} *are as described above,*

V_{Sn} = *volume (ml) of potassium dichromate solution required by the excess stannous chloride solution,*

and % Ferric iron is calculated as described above.

Because the ferric iron content of the sample is determined by difference, the reliability of the iron (III) result is directly dependent on the accuracy of the ferrous iron result. Any positive or negative error inherent in the iron (II) result, because of the presence of carbonaceous material, sulphides, or interfering elements in the sample, will produce a corresponding negative or positive error in the iron (III) result.

Calculations

Normality of ceric sulphate solution (N_{Ce}) $= \frac{N \times V}{v}$

where:

N = normality of the sodium oxalate (or ferrous ammonium sulphate) solution.

V = volume (ml) of the sodium oxalate (or ferrous ammonium sulphate) solution taken.

v = volume (ml) of ceric sulphate solution required by "V" ml of sodium oxalate (or ferrous ammonium sulphate) solution.

Iron equivalent (mg/ml) of the ceric sulphate solution (Fe_{EQ})

$$= N_{Ce} \times 55.85$$

$$\% \text{ Ferrous iron} = \frac{V \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V = volume (ml) of ceric sulphate solution required by the sample.

% FeO = 1.287 x % ferrous iron

Other applications

This method can be employed to determine ferrous iron in acid-soluble iron oxides and iron oxide ores and mill products. It is also applicable to carbonate rocks, clay, and shale in the absence of more than trace amounts of carbonaceous material.

References

1. Elsie M. Donaldson, Anal. Chem., 41, 501 (1969).
2. H.N.S. Schafer, Analyst, 91, 755, 763 (1966).
3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 907-922 (1953).
4. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 203-210 (1968).
5. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, 147, 150 (1957).
6. Idem, ibid., 133 (1957).
7. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 416-423 (1968).

DETERMINATION OF FERROUS IRON IN ACID-SOLUBLE IRON OXIDES AND IRON OXIDE ORES AND MILL PRODUCTS BY TITRATION WITH POTASSIUM DICHROMATE AFTER ACID-DECOMPOSITION IN AN AIR-FREE ATMOSPHERE

Principle

This method is based on the decomposition of the sample with hydrochloric and hydrofluoric acids in an air-free atmosphere. Ferrous iron is determined by titration with potassium dichromate, in an approximately 0.3 M sulphuric-0.2 M phosphoric acid medium, in the presence of sodium diphenylaminesulphonate as internal indicator, according to the reaction

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow$$
$$3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Outline

The sample is decomposed with hydrochloric and hydrofluoric acids in a nitrogen atmosphere, and the excess hydrofluoric acid is complexed with boric acid. The ferrous iron in the resulting solution is ultimately titrated with potassium dichromate solution.

Discussion of interferences

Elements that are present in the sample in lower oxidation states [e.g., vanadium (III), arsenic (III), antimony (III), titanium (III), copper (I), platinum, gold, uranium, molybdenum (III), molybdenum (V), and probably tungsten (III), and tungsten (V)] cause high results for ferrous iron because they either reduce any iron (III) that is released during sample decomposition, or because they are also oxidized by the potassium dichromate[1-4]. Other elements and compounds that interfere in the Potentiometric-Ceric Sulphate Method for ferrous iron (p 293) [i.e., vanadium (V), manganese (IV), carbonaceous material, pyrite, soluble sulphides, and metallic iron] interfere in this method in a similar manner.

Range

The method is suitable for samples containing more than approximately 0.5% of ferrous iron, but material containing lower concentrations can also be analyzed if more dilute (e.g., 0.02 N) potassium dichromate solution is employed as titrant.

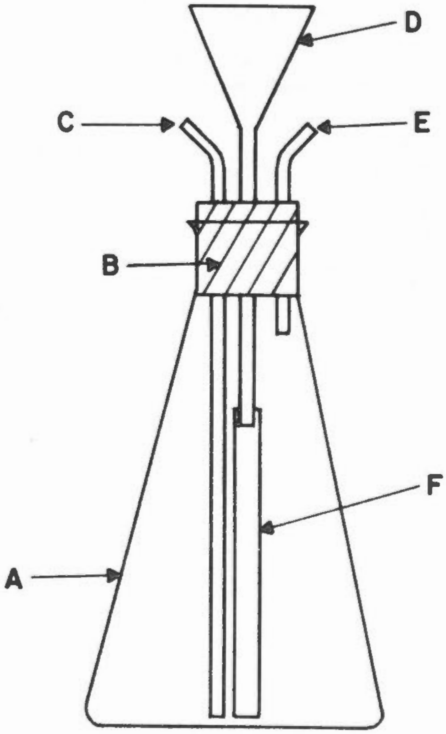

FIGURE 1. Apparatus for sample decomposition

A - Decomposition flask (250-ml Erlenmeyer-type).
B - Vinyl (Vikem) stopper.
C - Nitrogen-inlet tube [Nalgene (polypropylene or polycarbonate) tubing - inner and outer diameters approximately 2 mm and 5 mm, respectively] connected with rubber tubing to a nitrogen tank via a gas-control unit.
D - Nalgene funnel (approximately 10 ml capacity).
E - Nitrogen-outlet tube (Nalgene tubing).
F - Nalgene tubing.

Apparatus

Apparatus for sample decomposition. Illustrated in Figure 1.

Reagents

Standard potassium dichromate solution, 0.1 N. Prepare as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 276).

Ferrous ammonium sulphate solution, 0.1 N. Prepare as described in the above method for iron.

Sodium diphenylaminesulphonate (oxidized) indicator tablets (0.001 g) or oxidized solution. Prepare the solution as described in the above method for iron.

Boric acid solution, 5% w/v. Dissolve 50 g of the reagent in approximately 800 ml of hot water, cool, and dilute to 1 litre. Bubble nitrogen through the solution for 10-15 minutes, prior to use, to remove dissolved oxygen.

Hydrochloric acid (oxygen-free). Remove oxygen, prior to use, as described above.

Sulphuric acid, 50% v/v. Remove oxygen, prior to use, as described above.

Phosphoric acid, 50% v/v. Remove oxygen, prior to use, as described above.

Water (oxygen-free). Remove oxygen, prior to use, as described above.

Nitrogen (oxygen-free).

Standardization of potassium dichromate solution

Standardize the solution against pure iron as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure. Determine the normality of the potassium dichromate solution, and calculate the iron equivalent (mg/ml) (1 ml of 0.1 N potassium dichromate solution = 5.585 mg of iron).

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.25-1 g of powdered sample (Note 1), containing up to approximately 250 mg of ferrous iron, to the 250-ml Erlenmeyer decomposition flask A (Figure 1) (Note 2), and wash down the sides of the flask with water to dislodge any powder adhering to the inner walls. Assemble the apparatus, and add sufficient water through the funnel so that the nitrogen-inlet tube C and the acid-inlet tube F are approximately one-quarter inch below the surface of the water. Pass nitrogen into the apparatus for 3-4 minutes, at a flow rate of about 0.5 litre per minute, to remove dissolved air from the water and to displace the air in the apparatus.

Continue the flow of nitrogen, add 15 ml of concentrated oxygen-free hydrochloric acid through the funnel, swirl the apparatus - with both the nitrogen-inlet and acid-inlet tubes well below the surface of the solution - to disperse the sample, and heat the solution gently on a hot-plate until the decomposition of acid-soluble material is complete. Repeat the swirling process several times during the decomposition procedure (Note 3). Add 3-4 ml of concentrated hydrofluoric acid, continue heating the solution and, if necessary, repeat the addition of hydrochloric and hydrofluoric acids, in 5- and 2-ml portions, respectively, until the decomposition of insoluble material is complete (Note 4). Remove the apparatus from the hot-plate and place it in a cold water-bath. Add 40 ml of 5% oxygen-free boric acid solution through the funnel, and continue the flow of nitrogen until the solution has cooled to approximately room temperature. Stop the gas flow, remove the apparatus from the water-bath and, using oxygen-free water to wash the apparatus, transfer the sample solution, without delay, to a 600-ml beaker containing approximately 150 ml of oxygen-free water and 10 ml each of 50% oxygen-free sulphuric and phosphoric acids. Dilute the resulting solution to approximately 300 ml with oxygen-free water, add one sodium diphenylaminesulphonate indicator tablet (or 5 drops of indicator solution), and immediately proceed with the titration of the ferrous iron with 0.1 N potassium dichromate solution (Note 5) as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277) (Note 6). Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Notes

1. A sample that has been prepared by crushing, without grinding, in an agate (not iron or steel) mortar is preferable for the determination of ferrous iron. Fine grinding in air may result in considerable oxidation of ferrous iron in the sample because of the local heat generated during the grinding process[2].

2. A 250-ml clear Nalgene (polycarbonate) Erlenmeyer flask, if available, is preferable as a decomposition vessel because of the etching of the glass flask by hydrofluoric acid during the sample decomposition procedure. If a Nalgene flask is employed, sample decomposition should be carried out in a boiling water-bath to avoid heating the flask beyond its temperature limitations (approximately 135°C).

3. During sample decomposition, the solution should not be allowed to evaporate to the point where the nitrogen- and acid-inlet tubes are above the surface of the solution. If necessary, oxygen-free water should be added to maintain the volume of the solution at a suitable level.

4. The presence of a small amount of un-decomposed white or grayish-white siliceous residue will not cause significant error in the ferrous iron result. Yellow grains of un-decomposed pyrite in the residue indicate that the ferrous iron result will not be reliable. If there are more than a few grains of un-decomposed red to black-coloured material in the residue, heating should be continued until the decomposition of this material is complete.

5. Samples containing less than approximately 0.5% of ferrous iron can be analyzed at this stage by employing more dilute (e.g., 0.02 N) potassium dichromate solution for the titration. However, ferrous ammonium sulphate solution of the same normality should be employed for the determination of the reagent blank, as described in Note 6 (p 280) of the Volumetric-Stannous Chloride-Dichromate Method for total iron (1 ml of 0.02 N potassium dichromate solution = 1.117 mg of iron).

6. If the total iron content of the sample was not previously determined by the Volumetric-Stannous Chloride-Dichromate Method for total iron (Procedure A(a),p 277), the total iron, and subsequently the ferric iron content of the sample can be determined at this stage, as described in Note 8 (p 298) of the Potentiometric-Ceric Sulphate Method for ferrous iron, after the addition of 10 ml of concentrated hydrochloric acid to the solution obtained after the titration of ferrous iron, and evaporation of the solution to approximately 40 ml. The total iron and ferric iron contents of the sample are subsequently calculated as described in the above Note (p 298), except that for the total iron determination, the volume of potassium dichromate solution required for the titration is corrected for the reagent blank instead of an indicator blank.

Calculations

% Ferrous iron

$$= \frac{(V_S - V_B) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium dichromate solution required by the sample.

V_B = volume (ml) of potassium dichromate solution required by the blank.

Fe_{EQ} = iron equivalent (mg/ml) of the potassium dichromate solution.

% FeO = 1.287 x % ferrous iron

References

1. H.N.S. Schafer, Analyst, <u>91</u>, 755 (1966).

2. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 907-922 (1953).

3. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 203-210 (1968).

4. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, pp 178-179, 189, 192, 194 (1957).

DETERMINATION OF FERROUS IRON IN REFRACTORY IRON OXIDES AND IRON OXIDE ORES BY TITRATION WITH POTASSIUM DICHROMATE AFTER DECOMPOSITION IN A SEALED TUBE

Principle

This method is based on the decomposition of the sample with hydrochloric acid in a sealed tube filled with argon[1-3]. Ferrous iron is determined by titration with potassium dichromate, in an approximately 0.3 M sulphuric-0.2 M phosphoric acid medium, in the presence of sodium diphenylaminesulphonate as internal indicator, according to the reaction

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow$$

$$3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Outline

The sample is decomposed, at approximately 200°C, with hydrochloric acid in a sealed tube filled with argon. The ferrous iron in the resulting solution is ultimately titrated with potassium dichromate solution.

Discussion of interferences

All of the elements that interfere in the Volumetric-Dichromate Method for ferrous iron (p 301) either by reducing the iron (III) that is released during sample decomposition, or because they are oxidized by potassium dichromate [i.e., vanadium (III), arsenic (III), antimony (III), titanium (III), copper (I), platinum, gold, uranium, molybdenum (III), molybdenum (V), and probably tungsten (III), and tungsten (V)] interfere in this method in a similar manner. Other elements and compounds that interfere in both the Potentiometric-Ceric Sulphate (p 293) and the Volumetric-Dichromate Methods [i.e., vanadium (V), manganese (IV), carbonaceous material, pyrite, soluble sulphides, and metallic iron] also interfere in a similar manner. Pyrite, even in trace amounts, causes large positive errors in the ferrous iron result because, under the conditions of temperature and pressure that prevail during sample decomposition in the sealed tube, pyrite is completely or almost completely decomposed at the expense of the ferric iron in the sample. Soluble sulphides (e.g., pyrrhotite) cause even larger positive errors than pyrite because the hydrogen sulphide that is evolved in the sealed tube cannot escape, and subsequently reduces ferric iron, according to the reaction

$$H_2S + 4Fe_2O_3 \rightarrow 8FeO + H_2SO_4.$$

This reaction produces an amount of ferrous iron equivalent to approximately 14 times the amount of the sulphide sulphur present[4]. Metallic iron also causes larger positive errors than that resulting from the conversion of the iron to ferrous chloride during sample decomposition, because the hydrogen that is evolved during the reaction with hydrochloric acid reduces some of the iron (III) that is released during sample decomposition, according to the reaction

$$H_2 + 2FeCl_3 \rightarrow 2FeCl_2 + 2HCl.$$

Range

The method is suitable for samples containing more than approximately 1% of ferrous iron, but material containing lower concentrations can also be analyzed if more dilute (e.g., 0.02 N) potassium dichromate solution is employed as titrant.

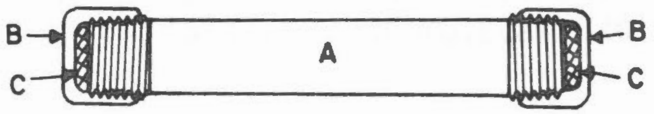

FIGURE 1. Protecting tube for the sealed decomposition tube

A - Galvanized iron pipe approximately 6 in. in length and threaded at both ends (inner and outer diameters approximately 16 mm and 20 mm, respectively).
B - Galvanized iron cap.
C - Glass-wool.

Apparatus

Protecting tube for the sealed decomposition tube. Illustrated in Figure 1. The glass-wool in the galvanized iron caps B protect the ends of the sealed tube from breakage during handling before and after sample decomposition.

Glass tubes for sample decomposition. These should be constructed from pyrex glass tubing with an inner diameter of approximately 7 mm, and a wall thickness of approximately 2.5 mm (Note 1), and should be 8-9 inches in length, and sealed at one end. Before use, the tubes should be thoroughly washed with hot 30% hydrochloric acid followed by water, and then dried in an oven at approximately 120°C.

Reagents

Standard potassium dichromate solution, 0.1 N. Prepare as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 276).

Ferrous ammonium sulphate solution, 0.1 N. Prepare as described in the above method for iron.

Sodium diphenylaminesulphonate (oxidized) indicator tablets (0.001 g) or oxidized solution. Prepare the solution as described in the above method for iron.

Hydrochloric acid (oxygen-free). Freshly boiled and cooled concentrated hydrochloric acid.

Hydrochloric acid (oxygen-free), 30% v/v. Prepare with oxygen-free concentrated hydrochloric acid and oxygen-free water.

Sulphuric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Phosphoric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Water (oxygen-free). Freshly boiled and cooled water.

Argon (oxygen-free).

Standardization of potassium dichromate solution

Standardize the solution against pure iron as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure. Determine the normality of the potassium dichromate solution, and calculate the iron equivalent (mg/ml) (1 ml of 0.1 N potassium dichromate solution = 5.585 mg of iron).

Procedure

In this procedure a reagent blank is carried along with the samples.

Using a small dry funnel, transfer 0.25-0.5 g of powdered sample (Note 2), containing up to approximately 250 mg of ferrous iron, to a dry decomposition tube that has been clamped in a vertical position. Carefully brush any powder adhering to the sides of the funnel into the neck of the funnel, then tap the neck of the funnel and the glass tube to dislodge any powder adhering to the walls, and wash the funnel with 0.5 ml of water. Using a small burner, carefully heat the mixture at the bottom of the tube to the boiling point for a moment to expel air from the powder, then remove the funnel and, using a narrow glass tube inserted to within 1.5-2 inches above the moistened sample, pass a slow stream of argon into the tube for 20-30 seconds to displace the air from the tube. Remove the narrow tube, and add 3 ml of concentrated oxygen-free hydrochloric acid through the funnel, then remove the funnel, and again displace the air from the tube with argon. Withdraw the narrow glass tube until it is within 1-1.5 inches below the top of the glass tube, continue the passage of a slow stream of argon (Note 3) and, using an air-propane flame, carefully seal the tube about 4-5 inches from the bottom (Note 4). Allow the sealed tube to cool, remove it from the clamp, and tip it horizontally several times to distribute the sample along most of its length.

Place the tube in a galvanized iron protecting tube (Figure 1) (Note 5) firmly capped at one end, and then loosely cap the open end (Note 6). Place the tube in a horizontal position in a muffle furnace maintained at approximately 200°C (Note 7), and heat for approximately 2 hours or preferably overnight. Remove the tube from the furnace, allow it to cool to room temperature, and remove the sealed tube. If sample decomposition is complete, or only a small amount of un-decomposed white or grayish-white residue remains (Note 8), file a groove around one end of the tube, approximately one-half inch from the end. Wash the outside of the tube and the groove thoroughly with 30% hydrochloric acid followed by water, to remove traces of metallic iron originating from the protecting tube and the file.

Using a small burner, apply heat to the groove, carefully break off the grooved short part of the tube and place it in an 800-ml beaker purged with argon and containing approximately 150 ml of oxygen-free water and 10 ml each of 50% oxygen-free sulphuric and phosphoric acids. Pour the solution in the remaining piece of tube into the beaker, and wash the inside of the tube thoroughly with 30% oxygen-free hydrochloric acid followed by oxygen-free water. Dilute the resulting solution to approximately 300 ml with oxygen-free water, add one sodium diphenylaminesulphonate indicator tablet (or 5 drops of indicator solution), and immediately proceed with the titration of the ferrous iron with 0.1 N potassium dichromate solution (Note 9) as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277) (Note 10). Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Notes

1. Glass tubes with a wall thickness of less than 2-2.5 mm should not be used because of the high pressures developed by concentrated hydrochloric acid in the sealed tube at temperatures above 100°C. Breakage may occur during sample decomposition, particularly if the glass is strained appreciably during the sealing process[1].

2. A sample that has been prepared by crushing, without grinding, in an agate (not iron or steel) mortar is preferable for the determination of ferrous iron. Fine grinding in air may result in considerable oxidation of ferrous iron in the sample because of the local heat generated during the grinding process[4].

3. During the sealing process, the flow of argon into the upper part of the tube should be as slow as possible. If too rapid a flow rate is employed, the pressure of the gas will cause the hot softened glass at the seal to bubble and blow out.

4. The tube can be sealed by constricting and drawing out the upper part of the tube, then working down the hot softened glass on the sealed tip until the desired thickness (i.e., 2-2.5 mm) and a hemispherical shape are obtained. Care must be taken that a minute capillary opening does not remain or else leakage will occur during the sample decomposition step. After the tube has cooled, the seal can be tested for capillary leakage by washing the tube with water, wiping it dry, and allowing it to stand in a vertical position with the sealed end resting on a piece of blue litmus paper. Leakage is indicated if the litmus paper exhibits an acid reaction[3].

5. The protecting tube prevents glass from scattering throughout the muffle furnace in the case of breakage resulting from excessive internal pressure in the sealed tube during the subsequent heating step. If a protecting tube is not employed, this would result in breakage of other sealed tubes if two or more samples are being decomposed simultaneously. The sealed tube can also be surrounded with solid calcium carbonate in the protecting tube. In case of breakage the calcium carbonate will neutralize the hydrochloric acid and prevent corrosion of the inside of the protecting tube[3].

6. The open end of the protecting tube should not be capped too tightly or else excessive "build-up" of pressure will occur in the tube, and may cause breakage of the sealed tube if the air inside the tube cannot escape during the heating stage.

7. The sealed tube should not be heated at temperatures exceeding approximately 250°C or else breakage may occur because of the high pressure developed by the hydrochloric acid inside the tube.

8. Any un-decomposed residue remaining in the sealed tube after the heating stage should be carefully examined with a hand lens. The presence of a small amount of un-decomposed white or grayish-white residue (i.e., silica, or titanium or zirconium oxides) will not cause significant error in the ferrous iron result. Yellow grains of un-decomposed pyrite in the residue indicate that the ferrous iron result will not be reliable. If there are more than a few grains of un-decomposed red to black-coloured material in the residue, the sealed tube should be replaced in the protecting tube, and heating should be continued until the decomposition of this material is complete.

9. Samples containing less than approximately 1% of ferrous iron can be analyzed at this stage by employing more dilute (e.g., 0.02 N) potassium dichromate solution for the titration. However, ferrous ammonium sulphate solution of the same normality should be employed for the determination of the reagent blank, as described in Note 6 (p 280) of the Volumetric-Stannous Chloride-Dichromate Method for total iron (1 ml of 0.02 N potassium dichromate solution = 1.117 mg of iron).

10. If sample decomposition was complete, and if the total iron content of the sample was not previously determined by the Volumetric-Stannous Chloride-Dichromate Method for total iron (Procedure A(a), p 277, and Note 8(b), p 281), the total iron, and subsequently the ferric iron content of the sample can be determined at this stage as described in Note 8 (p 298) of the Potentiometric-Ceric Sulphate Method for ferrous iron, after the addition of 25 ml of concentrated hydrochloric acid to the solution obtained after the titration of ferrous iron, and evaporation of the solution to approximately 40 ml. The total iron and ferric iron contents of the sample are subsequently calculated as described in the above Note (p 298), except that for the total iron determination, the volume of potassium dichromate solution required for the titration is corrected for the reagent blank instead of an indicator blank.

Calculations

$$\%\ \text{Ferrous iron} = \frac{(V_S - V_B) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium dichromate solution required by the sample.

V_B = volume (ml) of potassium dichromate solution required by the blank.

Fe_{EQ} = iron equivalent (mg/ml) of the potassium dichromate solution.

% FeO = 1.287 x % ferrous iron

References

1. E. Wickers, W.G. Schlecht and C.L. Gordon, J. Res. Natl. Bur. Std., 33, 363 (1944).
2. Idem, ibid., 33, 451 (1944).
3. C.L. Gordon, W.G. Schlecht and E. Wickers, ibid., 33, 457 (1944).

4. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 907-922 (1953).

DETERMINATION OF METALLIC IRON IN REDUCED IRON ORES AND SLAGS BY TITRATION WITH POTASSIUM DICHROMATE AFTER EXTRACTION WITH BROMINE-METHYL ALCOHOL SOLUTION

Principle

This method[1-3] is based on the selective conversion of metallic iron to the bromide by refluxing the sample with bromine-methyl alcohol solution. Iron is ultimately reduced to the divalent state with stannous chloride in a hydrochloric acid medium, and the excess of reductant is eliminated by oxidation with mercuric chloride. Metallic iron is determined by titration of the resultant iron (II) with potassium dichromate, in an approximately 0.3 M sulphuric-0.2 M phosphoric acid medium, in the presence of sodium diphenylaminesulphonate as internal indicator.

The corresponding reactions for these processes are:

$$2Fe + 3Br_2 \rightarrow 2FeBr_3$$

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2\downarrow$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl \rightarrow 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O.$$

Outline

The sample is refluxed with bromine-methyl alcohol solution, and iron (II) and iron (III) oxides and other insoluble material are removed by filtration. After removal of the bromine and methyl alcohol in the filtrate by evaporation, carbonaceous material is destroyed by evaporation with perchloric acid, and the salts are dissolved in hydrochloric acid. The iron in the resulting solution is ultimately reduced with stannous chloride and titrated with potassium dichromate solution.

Discussion of interferences

Iron carbide (Fe_3C) is soluble in the bromine-methyl alcohol solution employed for the dissolution of metallic iron, and causes high results for metallic iron because the iron from the carbide is subsequently oxidized by potassium dichromate[2,3]. Certain other iron compounds (e.g., silicides, sulphides, and phosphides) may interfere in a similar manner.

Range

The method is suitable for samples containing more than approximately 1% of metallic iron.

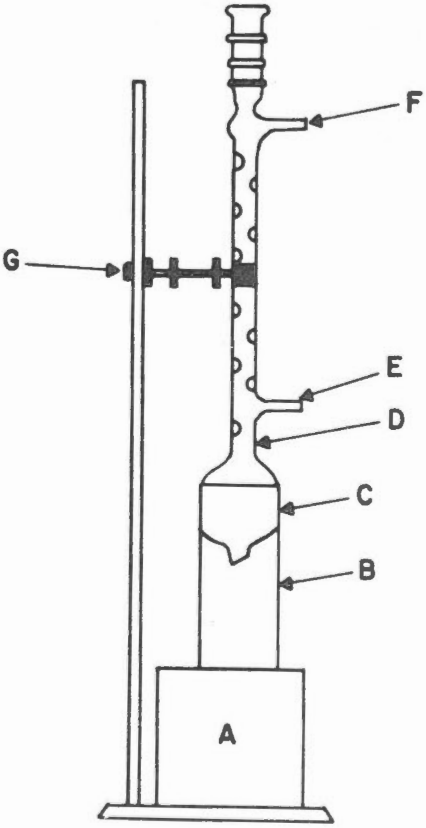

FIGURE 1. Apparatus for the extraction of metallic iron

A - Heating element.
B - Beaker (200-ml tall-form type).
C - Ground-glass joint.
D - Condenser (30-cm indented West-type).
E - Water-inlet.
F - Water-outlet.
G - Clamp.

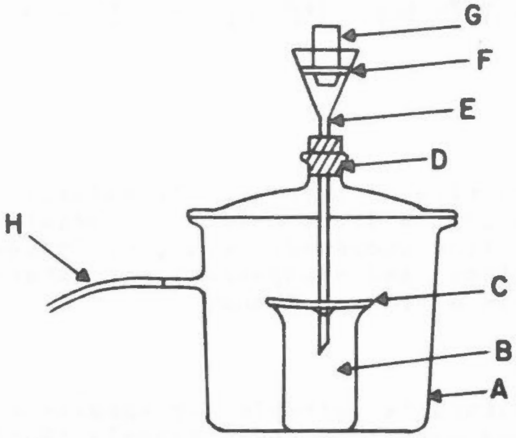

FIGURE 2. Filtration apparatus

A - Filtration jar (Witt-type).
B - Collecting beaker (400-ml).
C - Teflon cover with a hole drilled in the centre to accommodate the stem of the funnel.
D - Rubber stopper.
E - Funnel.
F - Crucible holder.
G - Crucible (25-ml Gooch-type).
H - Suction tube.

Apparatus

Apparatus for the extraction of metallic iron. Illustrated in Figure 1.

Filtration apparatus. Illustrated in Figure 2.

Reagents

Standard potassium dichromate solution, 0.1 N. Prepare as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 276).

Ferrous ammonium sulphate solution, 0.1 N. Prepare as described in the above method for iron.

Sodium diphenylaminesulphonate (oxidized) indicator tablets (0.001 g) or oxidized solution. Prepare the solution as described in the above method for iron.

Stannous chloride solution, 5% w/v. Prepare as described in the above method for iron.

Mercuric chloride solution, saturated.

Bromine-methyl alcohol solution, 5% v/v. Mix 10 ml of bromine with 200 ml of anhydrous methyl alcohol. Prepare fresh as required.

Hydrochloric acid, 10% v/v.

Sulphuric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Phosphoric acid (oxygen-free), 50% v/v. Prepare with oxygen-free water.

Water (oxygen-free). Freshly boiled and cooled water.

Methyl alcohol, anhydrous.

Standardization of potassium dichromate solution

Standardize the solution against pure iron as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure. Determine the normality of the potassium dichromate solution, and calculate the iron equivalent (mg/ml) (1 ml of 0.1 N potassium dichromate solution = 5.585 mg of iron).

Procedure

In this procedure a reagent blank is carried along with the samples.

Transfer 0.2-0.5 g of sample, ground to at least minus 100 mesh (Note 1), and containing up to approximately 200 mg of metallic iron, to a dry 200-ml tall-form beaker, and add several glass beads to prevent bumping. Start a flow of cold water in the condenser D (Figure 1), heat the electric heating element to 60-65°C, then add 50 ml of 5% bromine-methyl alcohol solution to the sample. Quickly attach the beaker to the condenser, and place it on the heating element (Note 2). Allow the mixture to reflux gently for 20 minutes (Note 3), then remove the beaker from the condenser, cover it with a watch glass, and quickly cool the solution to approximately room temperature in an ice-bath.

Assemble the filtration apparatus as shown in Figure 2, and insert two glass-fibre filter papers into a dry 25-ml Gooch crucible. Apply suction to the apparatus, and moisten the filter papers with anhydrous methyl alcohol. Add a small amount of glass-fibre filter pulp (Note 4) to the crucible, filter the sample solution as quickly as possible into the 400-ml collecting beaker, and wash the beaker thoroughly with anhydrous methyl alcohol (Notes 5 and 6). Wash the crucible and residue 8-10 times with anhydrous methyl alcohol, and remove the beaker containing the filtrate from the filtration jar.

Add 25 ml of concentrated hydrochloric acid and several glass beads to the filtrate, cover the beaker with a ribbed watch glass, place it in a hot water-bath, and carefully evaporate the solution to 15-20 ml to remove the bromine and methyl alcohol. Remove the beaker from the water-bath, add 25 ml of concentrated perchloric acid and evaporate the solution to dryness (Note 7). Cool, add 20 ml of concentrated hydrochloric acid and heat gently to dissolve the salts. Remove the watch glass, wash down the sides of the beaker with a small amount of 10% hydrochloric acid, and dilute the solution to approximately 30 ml with the same solution. Heat the resulting solution to just below the boiling point, and proceed with the stannous chloride reduction and subsequent titration of iron with 0.1 N potassium dichromate solution as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 277). Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Notes

1. Complete extraction of metallic iron may not be obtained by the described procedure if the sample is in a coarser state. If the sample has been subjected to oxidation (e.g., weathering), it is advisable to grind it to minus 200 mesh[2].

2. The refluxing and subsequent filtration of the sample solution must be carried out in a well-ventilated fume hood.

3. The sample should not be refluxed for less than 15 minutes or for more than approximately 30 minutes. Metallic iron may not be completely extracted if the reflux period is less than 15 minutes, and high results, presumably because of partial dissolution of iron oxides, may be obtained, particularly with samples of low metallic iron content, if the sample is refluxed for more than approximately 30 minutes[3].

4. If glass-fibre filter pulp is not available, it can be prepared by adding approximately 200 ml of anhydrous methyl alcohol to 8 or 10 glass-fibre filter papers in a dry 250-ml flask fitted with a ground-glass stopper, and shaking vigorously.

5. If required, the ferrous iron content of the sample can be determined at this stage as follows:

Transfer the residue quantitatively to the crucible, and after washing the crucible and residue as described, allow the residue to dry in air to remove the methyl alcohol. Moisten the residue with a small amount of water and, using a stirring rod, transfer the bulk of the residue and the glass-fibre filter papers and pulp to a 250-ml Erlenmeyer flask. Wash the crucible thoroughly with water to remove the remaining residue, and collect the washings in the flask containing the bulk of the residue. Wash down the sides of the flask with a small amount of water to dislodge any residue adhering to the inner walls, then proceed with the decomposition and subsequent titration of ferrous iron as described in the Volumetric-Dichromate Method for ferrous iron (p 302).

If the sample is known to be completely soluble in hydrochloric acid, the addition of hydrofluoric acid during the decomposition step, and the subsequent addition of boric acid solution to complex the excess hydrofluoric acid,may be omitted.

6. If the ferrous iron content of the sample was determined as described in Note 5, and the total iron content was previously determined by the Volumetric-Stannous Chloride-Dichromate Method for total iron (Procedure A(a), p 277), the ferric iron content

of the sample can be calculated as follows:

% Ferric iron = % total iron - (% metallic iron + % ferrous iron)

% Ferric iron expressed as Fe_2O_3 = 1.430 x % ferric iron.

7. Both low and moderate concentrations (up to approximately 5%) of metallic iron can be determined spectrophotometrically at this stage by the 1,10-Phenanthroline Method (p 55), after dissolution of the salts in water containing several drops of concentrated hydrochloric acid. Alternatively, up to approximately 10% can be determined by atomic-absorption spectrophotometry (p 3) after dissolution of the salts in dilute hydrochloric acid.

Calculations

% Metallic iron

$$= \frac{(V_S - V_B) \times Fe_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium dichromate solution required by the sample.

V_B = volume (ml) of potassium dichromate solution required by the blank.

Fe_{EQ}= iron equivalent (mg/ml) of the potassium dichromate solution.

References

1. G. Kraft and J. Fischer, Z. anal. Chem., 197, 217 (1963).

2. United States Steel Corporation Applied Research Laboratory, Physics and Analytical Chemistry Division, "Determination of Forms of Iron in Reduced Iron Ores and Agglomerates", File No. RM 2609.1, September (1970).

3. S.C. Blum and T.D. Searl, Anal. Chem., 43, 150 (1971).

DETERMINATION OF LEAD IN ORES AND MILL PRODUCTS BY THE IODOMETRIC METHOD AFTER PRECIPITATION AS LEAD CHROMATE

Principle

This method[1] is based on the conversion of insoluble lead sulphate to soluble lead acetate by treatment with sodium acetate-acetic acid solution, and the subsequent precipitation of lead as the chromate with potassium dichromate. The lead chromate precipitate is dissolved in dilute hydrochloric acid-sodium chloride solution, and chromium (VI) is reduced to the trivalent state with potassium iodide in an approximately 0.7 M hydrochloric acid medium. Lead is determined by titration of the resultant liberated iodine with sodium thiosulphate, in the presence of Thyodene (soluble starch) as internal indicator.

The corresponding reactions for these processes are:

$$PbSO_4 + 2NaC_2H_3O_2 \rightarrow Pb(C_2H_3O_2)_2 + Na_2SO_4$$

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O \rightarrow 2PbCrO_4 + 2KC_2H_3O_2 + 2CH_3COOH$$

$$PbCrO_4 + HCl \rightarrow PbCl_2 + H_2CrO_4$$

$$2H_2CrO_4 + 12HCl + 6Kl \rightarrow 2CrCl_3 + 6KCl + 8H_2O + 3I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI.$$

Outline

The sample is decomposed with hydrochloric, nitric, hydrofluoric and sulphuric acids. The solution is evaporated to fumes of sulphur trioxide and the resultant impure lead sulphate precipitate and the acid-insoluble material are ultimately separated by filtration.

If barium is absent, the lead sulphate in the resultant residue is converted to soluble lead acetate by digestion of the residue with sodium acetate-acetic acid solution, and the acid-insoluble material is removed by filtration. The lead in the filtrate is precipitated as the chromate with potassium dichromate and separated by filtration. After dissolution of the precipitate, and the addition of potassium iodide solution, the liberated iodine in the resulting solution is titrated with sodium thiosulphate solution.

If barium is present, the lead sulphate in the residue is converted to insoluble lead carbonate by digestion of the residue with ammonium carbonate solution. The lead carbonate and barium sulphate are removed by filtration, and the filtrate is combined with the initial filtrate. Lead carbonate is subsequently converted to soluble lead nitrate by treating the precipitate with dilute nitric acid, and the resultant solution is added to the combined filtrates. The remaining residue containing barium sulphate and acid-insoluble material is re-treated with ammonium carbonate solution to ensure the complete conversion of any remaining lead sulphate to lead carbonate, and the solution and precipitate are treated as described above. The lead in the combined filtrates is ultimately separated as the sulphate, converted to soluble lead acetate, precipitated as lead chromate, and determined as described above.

Discussion of interferences

Barium, mercury, and thallium interfere in the determination of lead, following its precipitation as the chromate from a dilute sodium acetate-acetic acid medium, because they also form insoluble chromates that react with potassium iodide to produce free iodine which is subsequently reduced by the sodium thiosulphate[1-4]. Silver and bismuth interfere in a similar manner because they form chromates that are partly insoluble in sodium acetate-acetic acid media.

Lead is separated from mercury and thallium, from the major portion of silver and bismuth, and from cadmium, iron, zinc, nickel, manganese, aluminum, magnesium, and vanadium by precipitation as the sulphate from a dilute sulphuric acid medium. Barium, calcium, strontium, and chromium contaminate the lead sulphate precipitate because they are completely or partly co-precipitated as insoluble sulphates. Tungsten, niobium, tantalum, and tin contaminate the precipitate because they are completely or partly co-precipitated as insoluble hydrolysis compounds[1-3]. Antimony is retained by the lead sulphate precipitate[1].

With the exception of barium, strontium, calcium, bismuth, and silver, lead is separated from moderate amounts of most of the above contaminating elements by converting the lead sulphate to lead acetate. Barium, strontium, calcium, and bismuth sulphates are partly soluble, and silver sulphate is completely soluble in the sodium acetate-acetic acid solution employed for the dissolution of the lead sulphate. Large amounts of barium and bismuth sulphates, and antimony and tin compounds interfere by preventing the complete dissolution of the lead sulphate with the acetate solution[1-3]. Large amounts of gelatinous silica interfere in a similar manner, but co-precipitation of silica with lead sulphate is avoided by removing the silica by volatilization as silicon tetrafluoride during sample decomposition.

Interference from antimony and tin can be avoided by volatilizing these elements as the bromides from a hydrobromic-sulphuric acid medium. Interference from barium is eliminated by converting the lead sulphate in the mixed lead and barium sulphate precipitate to lead carbonate by treatment of the precipitate with ammonium carbonate solution. The resultant mixed lead carbonate and barium sulphate precipitate is subsequently separated by filtration, and lead is separated from barium sulphate by dissolving the lead carbonate with dilute nitric acid; the lead is subsequently re-precipitated as the sulphate[2].

Strontium and calcium do not interfere in the precipitation and subsequent separation of lead as the chromate because they form chromates that are soluble in sodium acetate-acetic acid media[3]. Interference from small amounts of bismuth that are co-dissolved with the lead sulphate is avoided by complexing the bismuth with citric acid prior to the filtration of the lead chromate precipitate[1,2]. Milligram-quantities of silver, that may co-precipitate and be co-dissolved with the lead sulphate, do not cause significant error in the lead result because the co-precipitated silver chromate is partly soluble in the dilute sodium acetate solution employed to wash the lead chromate precipitate, and is subsequently removed, to a certain extent, during the washing step. Large amounts of silver, and probably large amounts of tungsten interfere in this method[1]. Moderate amounts of bismuth do not interfere.

Range

The method is suitable for samples containing more than approximately 0.2% of lead.

Reagents

Standard sodium thiosulphate solution, 0.1 N. Prepare as described in the Volumetric-Iodometric Method for copper (p 256).

Standard potassium dichromate solution (1 ml = 5 mg of potassium dichromate). Dissolve 0.5000 g of pure pulverized reagent (dried at 105°C for 1-2 hours) in water and dilute to 100 ml.

Thyodene (soluble starch) indicator solution, 5% w/v. Dissolve 5 g each of Thyodene and potassium iodide in water and dilute to 100 ml. Prepare fresh as required.

Potassium iodide solution, 20% w/v. Prepare fresh as required.

Sodium chloride solution, saturated.

Sodium acetate solution, saturated. Filter the solution, if necessary.

Sodium acetate-acetic acid solution. Add 25 ml of concentrated acetic acid to 325 ml of saturated sodium acetate solution, and dilute to 1 litre with water.

Hydrochloric acid-sodium chloride solution. Add 150 ml each of water and concentrated hydrochloric acid to 1000 ml of saturated sodium chloride solution and mix thoroughly.

Potassium dichromate solution, saturated.

Ammonium carbonate solution, saturated.

Sodium acetate wash solution. Add 50 ml of saturated sodium acetate solution to 1000 ml of water and mix thoroughly.

Sulphuric acid, 50%, 10%, and 1% v/v.

Nitric acid, 10% v/v.

Standardization of sodium thiosulphate solution

Transfer a 20-ml aliquot of the standard potassium dichromate solution (Note 1) to a 300-ml Erlenmeyer flask and add approximately 50 ml of water. Add 6 ml of concentrated hydrochloric acid and dilute the solution to approximately 90 ml with water. Add 10 ml of freshly prepared 20% potassium iodide solution (Note 2), mix gently and, while swirling the flask, immediately titrate the solution with standard sodium thiosulphate solution until the brown colour of the liberated iodine has almost disappeared and the solution is yellowish-green. Add 5 ml of 5% Thyodene solution and carefully continue the titration, by drops, until the blue-starch iodine colour has completely disappeared and the solution is clear green (Note 3). Determine the normality of the sodium thiosulphate solution, and calculate the lead equivalent (mg/ml) (1 ml of 0.1 N sodium thiosulphate solution = 6.906 mg of lead) (Note 4).

Alternatively, the sodium thiosulphate solution can be standardized against pure copper metal as described in the Volumetric-Iodometric Method for copper (p 257).

Procedure

Barium absent

Transfer 0.1-2 g of powdered sample, containing up to approximately 100 mg of lead, to a 250-ml Teflon beaker. Add 10 ml of concentrated hydrochloric acid, cover the beaker with a Teflon cover, and boil for several minutes. Add 10 ml of concentrated nitric acid and 5 ml of concentrated hydrofluoric acid, boil until the decomposition of acid-soluble material is complete (Note 5), then add 12 ml of 50% sulphuric acid, remove the cover (Note 6), and evaporate the solution to fumes of sulphur trioxide (Note 7). Cool, wash down the sides of the beaker with water, evaporate the solution to fumes again, then repeat the washing and evaporation steps to ensure the complete removal of nitric, hydrochloric, and hydrofluoric acids (Note 8). Cool, add approximately 50 ml of water, heat gently to dissolve the soluble salts, and dilute the solution to approximately 100 ml with water (Notes 9 and 10). Cool the solution below room temperature and allow it to stand for approximately 1 hour. Filter the solution (Whatman No. 42 paper) into a 400-ml pyrex beaker, wash the beaker (Note 11), paper, and precipitate thoroughly with cold 1% sulphuric acid (Note 12), then wash the paper and precipitate once with cold water (Note 13).

Place a 250-ml beaker under the funnel, punch a hole in the bottom of the filter paper with a pointed glass rod, and wash the impure lead sulphate precipitate into the beaker with a minimum amount of hot water. Wash the paper, including the inside flap, with a small amount of hot water, transfer it to the original Teflon beaker, and wash the funnel with a small amount of hot water. Wash down the sides of the Teflon beaker with 25 ml of hot sodium acetate-acetic acid solution, macerate the paper thoroughly with a glass rod, and digest the mixture on a hot-plate for 15-20 minutes. Filter the mixture (Whatman No. 40 paper) into the beaker containing the impure lead sulphate precipitate, and wash the beaker, paper, and residue thoroughly with small portions of hot sodium acetate-acetic acid solution. Discard the paper and residue. Wash the funnel with a small amount of hot water, and heat the solution until all of the lead sulphate has dissolved (Note 14). Filter the solution (Whatman No. 40 paper) into a 300-ml Erlenmeyer flask, and wash the beaker, paper, and residue with small portions of hot water. Discard the paper and residue.

Dilute the resulting solution to approximately 150 ml with water, heat to the boiling point and, by pipette, slowly add 10 ml of saturated potassium dichromate solution. Boil the solution gently for 5-10 minutes, or until the yellow colour of the resultant lead chromate precipitate changes to red (Notes 15 and 16). Allow the precipitate to settle until the supernatant solution is clear (Note 17), then filter the solution (Whatman No. 42 paper) and wash the flask (Note 11), paper, and precipitate 10 times with 10-ml portions of hot dilute sodium acetate wash solution, or until all traces of excess potassium dichromate solution have been removed from the filter paper. Discard the filtrate.

Place the Erlenmeyer flask that contained the precipitate under the funnel and, using 5-10-ml portions, dissolve the lead chromate precipitate with 25 ml of cold hydrochloric acid-sodium chloride solution. Using a wash bottle, wash the paper, including the inside flap, with a further 15-ml portion of the same solution, then, using 5-10-ml portions, wash the paper thoroughly with 40 ml of cold water to remove all of the yellow colour. Discard the paper. Wash down the sides of the flask with 10 ml of the hydrochloric acid-sodium chloride solution, add 10 ml of 20% potassium iodide solution, mix gently, and immediately proceed with the titration of the liberated iodine as described above.

<u>Barium present</u>

Following sample decomposition as described above, and filtration of the impure lead sulphate precipitate (Note 18), wash the paper and precipitate with 1% sulphuric acid (Note 12) as described, then 3 or 4 times with cold water to remove the excess sulphuric acid. Retain the filtrate and, using a jet of water, transfer the precipitate, as quantitatively as possible, to a 250-ml beaker. Retain the filter paper.

Evaporate the solution containing the precipitate to approximately 5 ml, add 3 or 4 drops of concentrated ammonium hydroxide and 30 ml of saturated ammonium carbonate solution, cover the beaker, and boil the solution gently (Note 19) for approximately 10 minutes. Filter the hot solution (Whatman No. 40 paper) into the beaker containing the initial filtrate (Note 20), and wash the beaker, paper, and precipitate thoroughly with cold water to remove ammonium sulphate. Cover the funnel with a watch glass (Note 21), dissolve the lead carbonate precipitate with 20 ml of 10% nitric acid, and collect the solution in the 400-ml beaker containing the combined filtrates and washings. Wash the watch glass, paper, and residue thoroughly with 10% nitric acid, then wash the paper and residue 3 or 4 times with water to remove excess nitric acid.

Transfer the paper and residue to the 250-ml beaker that contained the impure lead sulphate precipitate, and wash the funnel with a small amount of water. Add 5 ml of water, 3 or 4 drops of concentrated ammonium hydroxide, and 15 ml of saturated ammonium carbonate solution to the beaker containing the paper and residue. Macerate the paper thoroughly with a glass rod, cover the beaker, and digest the mixture on a hot-plate for approximately 15 minutes. Filter the mixture (Whatman No. 40 paper) into the 400-ml beaker containing the initial filtrate, the filtrate from the initial lead carbonate separation, and the dissolved lead carbonate, and wash the beaker, paper, and residue thoroughly with cold water, then with 10% nitric acid. Discard the paper and residue.

Add 2 ml of 50% sulphuric acid and 15 ml of concentrated hydrochloric acid to the resulting solution, cover the beaker, boil vigorously to decompose the ammonium salts, then remove the cover and evaporate the solution to fumes of sulphur trioxide (Note 7). Cool, wash down the sides of the beaker with water, evaporate the solution to fumes of sulphur trioxide again, then repeat the washing and evaporation steps to ensure the complete removal of hydrochloric and nitric acids. Cool, add approximately 50 ml of water, heat gently to dissolve the salts, and dilute the solution to approximately 100 ml with water (Notes 9 and 10). Cool the solution below room temperature, allow it to stand for 1 hour, then, using the same filter paper that was employed for the filtration of the initial impure lead sulphate precipitate, proceed with the filtration and washing of the resultant impure lead sulphate precipitate (Note 22); the treatment of the filter paper with sodium acetate-acetic acid solution in the original Teflon beaker; the dissolution of the lead sulphate precipitate with the sodium acetate-acetic acid solution; the precipitation of lead chromate; and the subsequent titration of the liberated iodine as described above.

Notes

1. Because the separation of lead as the sulphate from dilute sulphuric acid media is not quite quantitative (Note 13), standardization of the sodium thiosulphate solution against pure lead metal (e.g., 0.1 g), dissolved in concentrated nitric acid and carried through the initial procedure described, is recommended in routine work to minimize error resulting from the solubility of lead sulphate. A 0.1000-g portion of lead theoretically requires 14.48 ml of 0.1 N sodium thiosulphate solution. The lead equivalent (mg/ml) of the sodium thiosulphate solution can subsequently be determined by direct calculation. In exact work (Note 13), the sodium thiosulphate solution should be standardized against pure potassium dichromate or, alternatively, against pure copper metal as described.

2. The solution should be titrated immediately after the addition of potassium iodide solution to prevent error resulting from the loss of iodine by volatilization, and from the liberation of iodine by air-oxidation of iodide ion, according to the reaction

$$4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O.$$

The rate of air-oxidation of iodide ion is increased by increased acidity and by sunlight. Consequently, the titration should not be performed in direct sunlight, and solutions containing iodide should be prepared just before use or kept in brown bottles[5]. Alternatively, 2 g of solid potassium iodide can be employed instead of a 20% solution.

The reactions for the processes involved in the standardization of sodium thiosulphate solution with potassium dichromate are

$$K_2Cr_2O_7 + 6KI + 14HCl \rightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI.$$

3. A sheet of white paper placed under the flask assists in the recognition of the end-point. A 20-ml portion of the potassium dichromate solution (i.e., 100 mg) requires 20.39 ml of 0.1 N sodium thiosulphate solution.

4. Because sodium thiosulphate solutions slowly change in concentration on standing, the standard solution should be re-standardized periodically. If the concentration has decreased by more than approximately 1%, a fresh solution should be prepared. Once decomposition has started, it generally proceeds rapidly[6].

5. Additional hydrochloric acid may be required at this stage to dissolve precipitated lead chloride.

6. If the sample contains antimony and/or an appreciable amount of tin, proceed as follows:

Add 10 ml of concentrated hydrobromic acid and evaporate the solution to fumes of sulphur trioxide (Note 7). Cool, wash down the sides of the beaker with water, add a further 10-ml portion of hydrobromic acid, evaporate the solution to fumes again, then proceed as described.

Arsenic and some mercury are also volatilized as the bromides by the above procedure.

7. If the sample contains bismuth, the solution should be fumed at a relatively low temperature (approximately 250°C) to minimize the co-precipitation of bismuth with lead sulphate. Bismuth is heavily co-precipitated if the solution is fumed strongly at high temperatures (e.g., 350-400°C)[3].

8. Low results will be obtained for lead if the excess nitric and hydrochloric acids are not completely expelled from the solution[2].

9. If the sample contains tin, which was not previously removed by volatilization as the bromide (Note 6), the solution should be filtered without delay after dilution with water. On standing, stannic sulphate tends to hydrolyze and form insoluble compounds that contaminate the lead sulphate

precipitate, and may subsequently prevent the complete dissolution of the lead sulphate in sodium acetate-acetic acid solution[1-3].

10. The loss of lead resulting from the slight solubility of lead sulphate in dilute sulphuric acid media (Note 13) can be reduced to negligible proportions by diluting the solution to 100 ml with ethyl or methyl alcohol at this stage. However, this procedure is not recommended for samples that contain elements that form sparingly soluble sulphates [e.g., iron (III), chromium and, particularly bismuth, calcium, strontium, and silver] because of the resultant increased contamination of the lead sulphate precipitate[1-3]. This may result in incomplete separation of lead from the impure lead sulphate precipitate during the subsequent treatment of the precipitate with sodium acetate-acetic acid solution.

11. It is not necessary to transfer the precipitate quantitatively to the filter paper.

12. If the sample contains an appreciable amount of bismuth and/or iron, the precipitate should be washed with 10% sulphuric acid to maintain bismuth in solution, and to prevent the formation of the difficultly soluble basic ferric sulphate[2].

13. According to data on the equilibrium solubility of lead sulphate in solutions of sulphuric acid[7], approximately 0.5 mg of lead, for each 100 mg in the sample, remains in the filtrate when lead sulphate is precipitated from an approximately 5% sulphuric acid medium[8]. In exact work, the small amount of lead remaining in the filtrate can be determined by atomic-absorption spectrophotometry and added to the result obtained, following evaporation of the filtrate to 1-2 ml; dissolution of the soluble salts in concentrated nitric acid; conversion of lead sulphate to lead carbonate by treatment with ammonium carbonate in an ammoniacal medium; separation of the mixed hydrous oxide of lead and lead carbonate by occlusion with hydrous ferric oxide; and subsequent conversion to soluble lead nitrate, as described in the atomic-absorption spectrophotometric method for the determination of lead in sulphide ores and mill products (p 19).

14. Additional sodium acetate-acetic acid solution may be required to dissolve all of the lead sulphate. However, the resulting solution should not contain more than approximately 75 ml of this solution, prior to the precipitation of lead chromate[1].

15. The crystalline red or orange compound is of definite composition and may be quickly filtered and washed. The yellow precipitate is of indefinite composition, yields high results for lead, and is difficult to wash[2].

16. If the sample contains bismuth, or bismuth is not known to be absent, add 2 g of citric acid to the resulting solution to complex bismuth, and stir to dissolve, prior to the filtration of the lead chromate[1,2].

17. If sufficient potassium dichromate is present, the supernatant solution should be yellow.

18. The precipitate containing the lead and barium sulphates should be transferred, as quantitatively as possible, to the filter paper. Reserve the Teflon beaker for the sodium acetate-acetic acid treatment of the filter paper after the subsequent second filtration of the impure lead sulphate precipitate (Note 22) through the same filter paper.

19. To prevent rapid decomposition of the ammonium carbonate and, consequently, incomplete conversion of the lead sulphate to lead carbonate, the solution should not be boiled too vigorously at this stage.

20. The filtrate is combined with the initial filtrate to avoid loss of lead resulting from the slight solubility of lead carbonate in the ammonium sulphate solution which is produced during the conversion of lead sulphate to lead carbonate by treatment with ammonium carbonate solution[2].

21 The funnel should be covered to avoid loss of lead by spraying during the subsequent decomposition of the lead carbonate with dilute nitric acid.

22. By combining the initial filtrate from the impure lead sulphate precipitate with the filtrates from the lead carbonate separation, and by dissolving the lead carbonate into the same solution, followed by re-evaporation of the solution to fumes of sulphur trioxide and re-precipitation of the impure lead sulphate, a second loss of lead, resulting from the solubility of lead sulphate in dilute sulphuric acid medium (Note 13), is avoided.

Calculations

Normality of sodium thiosulphate solution (N_{NaTS})

$$= \frac{\text{Weight of potassium dichromate in aliquot taken (g)}}{0.04904 \times V}$$

where:

V = volume (ml) of sodium thiosulphate solution required by the iodine liberated by the potassium dichromate.

Lead equivalent (mg/ml) of the sodium thiosulphate solution (Pb_{EQ})

$$= N_{NaTS} \times \frac{1}{3} \times 207.2$$

$$\% \text{ Pb} = \frac{V_S \times Pb_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of sodium thiosulphate solution required by the sample.

Other applications

This method can be employed to determine lead in copper- and zinc-base alloys.

References

1. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 223-227, 229-230 (1953).
2. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 556-561, 562, 566-568 (1962).
3. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 6, pp 96, 99, 110-113, 124 (1964).
4. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, pp 335-338 (1957).
5. Idem, ibid., 203 (1957).
6. Idem, ibid., pp 225-230 (1957).
7. D.N. Craig and G.W. Vinal, J. Res. Natl. Bur. Std., 22, 55 (1939).
8. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 6, 153 (1964).

DETERMINATION OF MANGANESE IN MANGANESE AND IRON ORES AND MILL PRODUCTS BY POTENTIOMETRIC TITRATION WITH POTASSIUM PERMANGANATE

Principle

This method[1,2] is based on that developed by Lingane and Karplus[3], and involves the oxidation of manganese (II) to the trivalent state with potassium permanganate in a weakly acid (pH 6.5) medium. Manganese is determined by potentiometric titration in the presence of pyrophosphate ion (0.2-0.3 M), which forms a stable, intensely coloured, reddish-violet complex with the manganese (III) produced, according to the reaction

$$4Mn^{+2} + MnO_4^{-} + 8H^{+} + 15H_2P_2O_7^{-2} \rightarrow 5Mn(H_2P_2O_7)_3^{-3} + 4H_2O.$$

Outline

The sample is decomposed with hydrochloric, nitric, and perchloric acids, and the solution is evaporated to fumes of perchloric acid to oxidize various sample components and to dehydrate silica. The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate, the melt is dissolved in the initial filtrate, and chromium, if present, is removed by volatilization as chromyl chloride. The manganese in the resulting solution is ultimately titrated with potassium permanganate solution.

Discussion of interferences

Most of the elements or substances that interfere in this method by oxidizing manganese (II) [e.g., chlorine and chromium (VI)] or by reducing permanganate ion [e.g., oxides of nitrogen, iron (II), vanadium (IV), and cerium (III)][3-5] are removed or oxidized during sample decomposition by evaporation of the solution with perchloric acid. Interference from chromium (VI) is avoided by volatilizing it as chromyl chloride from a hydrochloric-perchloric acid medium. Vanadium (V) and cerium (IV), if present in the sample or produced during sample decomposition, partly oxidize manganese (II) to the trivalent state. However, large amounts of these ions (approximately 50-60 times the amount of manganese present) do not interfere in the determination of manganese because the resultant vanadium (IV) and cerium (III) are subsequently reoxidized by potassium permanganate during the titration procedure[4,5].

Large amounts of chloride, sulphate, nitrate, chlorate, perchlorate, arsenate, iron (III), cobalt, nickel, copper, zinc, cadmium, aluminum, magnesium, tin, antimony, lead, chromium (III), molybdenum (VI), tungsten (VI), and uranium (VI) do not interfere[3-5].

Range

The method is suitable for manganese ores and mill products, and iron ores and mill products containing more than approximately 0.8 and 0.4% of manganese, respectively.

Apparatus

Apparatus for the potentiometric titration of manganese. Illustrated in Figure 1 (p 250) of the Potentiometric-Ferrous Ammonium Sulphate Method for chromium.

Reagents

Standard potassium permanganate solution, 0.1 N. Prepare as described in the Volumetric-Oxalate Method for calcium (p 242).

Hydrogen peroxide, 3% w/v. Dilute 10 ml of 30% hydrogen peroxide to 100 ml with water.

Sodium hydroxide solution, 20% w/v. Prepare fresh as required (Note 1).

Sodium pyrophosphate solution, saturated (Note 2).

Hydrochloric acid, 50% and 10% v/v.

Sulphuric acid, 50% v/v.

Standardization of potassium permanganate solution

Standardize the solution against pure sodium oxalate as described in the Volumetric-Oxalate Method for calcium (p 242). Correct the result obtained by subtracting that obtained for a blank that is carried through the same procedure. Determine the normality of the potassium permanganate solution, and calculate the manganese equivalent (mg/ml) (1 ml of 0.1 N potassium permanganate solution = 4.395 mg of manganese) (Note 3).

Alternatively, the potassium permanganate solution can be standardized against a sample of manganese ore of known manganese content, by carrying the sample through the described procedure, and the manganese equivalent can be determined by direct calculation.

Procedures

In these procedures a reagent blank is carried along with the samples.

Manganese ores and mill products

Transfer 0.2-0.5 g of powdered sample, containing up to approximately 200 mg of manganese, to a 250-ml beaker, and add 10 ml each of concentrated hydrochloric and nitric acids, and 15 ml of concentrated perchloric acid. Cover the beaker, heat gently until the decomposition of acid-soluble material is complete, then evaporate the solution to fumes of perchloric acid, and continue fuming for approximately 10 minutes (Note 4). Cool, add 50 ml of water and heat gently to dissolve the soluble salts (Note 5). Filter the resulting solution (Whatman No. 42 paper) into a 600-ml beaker, transfer the residue quantitatively to the filter paper, and wash the paper and residue with hot 10% hydrochloric acid, then thoroughly with hot water to remove perchlorates.

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 800°C. Cool the crucible, and add 1 ml each of concentrated nitric acid and 50% sulphuric acid, and 5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid. Fuse the residue with 1-2 g of sodium carbonate, allow the melt to cool, then transfer the crucible and contents to the beaker containing the initial filtrate, and add 5 ml of concentrated hydrochloric acid in small increments. When dissolution of the melt is complete, remove the crucible after wash-it thoroughly with hot water, and evaporate the solution to fumes of perchloric acid.

Cover the beaker and, if chromium is present, add concentrated hydrochloric acid in small increments, and evaporate the solution to fumes of perchloric acid after the addition of each increment until no further chromyl chloride (i.e., orange vapour) is expelled. Evaporate the resulting solution to 2-3 ml, or until the sodium salts begin to crystallize. Cool, add 10 ml of 50% hydrochloric acid and 1 ml of 3% hydrogen peroxide, and boil the solution for 4-5 minutes to expel hydrogen peroxide. Add 250-300 ml of cold saturated sodium pyrophosphate solution, then, using a pH meter, adjust the pH of the resulting solution to 6.5 (Note 6) with 20% sodium hydroxide solution, and concentrated hydrochloric acid, if required (Note 7). Cool the solution to 10-20°C, and titrate the manganese potentiometrically (Note 8) with 0.1 N potassium permanganate solution. Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Iron ores and mill products

Transfer 1 g of powdered sample to a 250-ml beaker and add 30 ml of concentrated hydrochloric acid. Cover the beaker, and heat gently, without boiling, until the decomposition of acid-soluble material is complete. Add 10 ml of concentrated nitric acid and 15 ml of concentrated perchloric acid, and evaporate the solution to fumes of perchloric acid. Continue fuming for approximately 10 minutes, then proceed with the filtration, the decomposition of the residue, the volatilization of chromium, if present, and the subsequent titration of manganese as described above.

Notes

1. The sodium hydroxide solution employed should be free of reducing substances; these are present if a green colour, indicating the reduction of permanganate ion to manganate ion, is formed on the addition of 1 drop of 0.1 N potassium permanganate solution to a 10-ml portion of the sodium hydroxide solution[3].

2. Because pyrophosphate ion slowly hydrolyzes in cold neutral solutions, solutions of sodium pyrophosphate that are more than 2-3 weeks old should not be employed. Some batches of the reagent contain impurities that cause erratic potential readings and yield high blanks. Each new batch should be tested by using it in the titration of a known amount of manganese, and only batches which rapidly provide steady potentials should be employed[3].

3. The apparent concentration (i.e., 0.1 N) of the potassium permanganate solution employed is based on the usual valence change of manganese in acid solution from 7 to 2. Although this concentration applies in the titration of sodium oxalate, according to the reaction

$$2K\overset{(+7)}{Mn}O_4+5Na_2C_2O_4+8H_2SO_4\uparrow,$$

$$\rightarrow K_2SO_4+2\overset{(+2)}{Mn}SO_4+5Na_2SO_4+8H_2O+10CO_2\uparrow,$$

the actual normality of the solution for the reaction involved in this method is 0.08 (i.e., 4/5 x 0.1) because manganese (VII) is reduced to manganese (III) - a valence change of 4 instead of 5 - during the oxidation of manganese in the sample from the divalent to the trivalent state. Consequently, the manganese equivalent of the potassium permanganate solution employed = 0.1 x 4/5 x 54.94 mg of manganese per ml.

4. The sample solution must be fumed strongly with perchloric acid to ensure the complete oxidation of various sample constituents, particularly vanadium.

5. If some manganese has separated as manganese dioxide, add 2-3 drops of 3% hydrogen peroxide at this stage to dissolve the brown dioxide, then boil the solution for approximately 4-5 minutes to remove excess hydrogen peroxide.

6. Although the titration can be performed successfully at pH values between approximately 1 and 8, the potential break at the equivalence point is maximal when the pH of the solution is between 6 and 7. Below pH 6 the magnitude of the potential break decreases considerably. Above pH 8 no break is observed at the point corresponding to the oxidation of manganese to the trivalent state, because the pyrophosphate complex of manganese (III) is unstable and disproportionates into hydrous manganese dioxide and manganese (II)[3].

7. The solution should be clear and colourless at this stage. If a pink colour due to permanganate ion is observed, the solution should be discarded and the analysis repeated. If a white precipitate (i.e., manganous pyrophosphate) forms, clarify the solution, while maintaining a pH of 6.5, by adding more sodium pyrophosphate solution.

8. With relatively pure manganese solutions and a sodium pyrophosphate concentration between 0.2-0.3 M, the equivalence point potential, at pH 6-7, is approximately +0.47 volt vs. the saturated calomel electrode. A slightly lower value is usually found in the presence of large amounts of other metal ions, The magnitude of the potential change at the equivalence point (i.e., the maximal value of $\Delta E/\Delta V$) is between 100 and 200 millivolts per 0.1 ml of potassium permanganate solution[3].

Calculations

Manganese equivalent (mg/ml) of the potassium permanganate solution $(Mn_{EQ}) = N \times \frac{4}{5} \times 54.94$

where:

N = normality of the potassium permanganate solution.

$$\% \ Mn = \frac{(V_S - V_B) \times Mn_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium permanganate solution required by the sample.

V_B = volume (ml) of potassium permanganate solution required by the blank.

% MnO = 1.291 x % Mn

Other applications

With modifications in the decomposition procedure, this method can be employed to determine manganese in ferromanganese, silicomanganese, speigeleisen, cast iron, steel, and bronze[3].

References

1. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E 248-68, pp 748-750 (1971).

2. Idem, ibid., Part 32, E 314-71, pp 804-807 (1971).

3. J.J. Lingane and R. Karplus, Ind. Eng. Chem., Anal. ed. 18, 191 (1946).

4. G. Goffart, G. Michel and Th. Pitance, Anal. Chim. Acta, 1, 393 (1947).

5. I.M. Kolthoff and E. Jacobsen, Microchem. Jour., 1, 3 (1957).

DETERMINATION OF MOLYBDENUM IN MOLYBDENUM ORES AND MILL PRODUCTS BY TITRATION WITH POTASSIUM PERMANGANATE AFTER REDUCTION IN A JONES REDUCTOR

Principle

This method[1-3] is based on the reduction of molybdenum to the trivalent state, in an approximately 1 M sulphuric acid medium, by passing the solution through a column of amalgamated zinc. The reduced compound, which is susceptible to air-oxidation, is collected in a nitrogen atmosphere in a solution containing an excess of ferric sulphate. Molybdenum is determined by titration of the resultant iron (II) and molybdenum (V) [formed during the reaction of molybdenum (III) with ferric sulphate] with potassium permanganate.

The corresponding reactions for these processes are:

$$\mathrm{2MoO_4^{-2} + 3Zn + 16H^+ \rightarrow 2Mo^{+3} + 3Zn^+ + 8H_2O}$$

$$\mathrm{Mo^{+3} + 2Fe^{+3} \rightarrow Mo^{+5} + 2Fe^{+2}}$$

$$\mathrm{5Mo^{+5} + 10Fe^{+2} + 24H^+ + 3MnO_4^- \rightarrow 5Mo^{+6} + 10Fe^{+3} + 3Mn^{+2} + 12H_2O.}$$

Outline

Molybdenite ores and mill products are decomposed with nitric and sulphuric acids, and the solution is evaporated to fumes of sulphur trioxide to remove excess nitric acid. The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate, and the melt is dissolved in the initial filtrate. Chromium (VI), if present, is reduced with hydrogen peroxide, and chromium (III), iron, arsenic, and certain other interfering elements (titanium, uranium, niobium, and some antimony and tin) are precipitated as the hydrous oxides with ammonium hydroxide, and separated from molybdenum by filtration. After dissolution of the precipitate, the hydrous oxides are re-precipitated twice to recover the occluded molybdenum, and the filtrates are combined with the initial filtrate.

If tungsten, nickel, and vanadium are absent, the combined filtrates are acidified with perchloric acid, and the excess ammonium salts are decomposed by treatment with nitric and hydrochloric acids. After removal of nitric acid by evaporation with sulphuric acid, copper, if present, is ultimately reduced to the metallic state with zinc metal, and separated from molybdenum by filtration. The molybdenum in the resultant filtrate, or the preceding solution if copper is absent, is ultimately reduced by passing the solution through the Jones reductor, and the solution is collected in a solution containing excess ferric sulphate. The molybdenum (V) and iron (II) in the resulting solution are titrated with potassium permanganate solution.

If tungsten, nickel, and/or vanadium are present, some nickel and platinum and certain other elements (zinc, cobalt, and cadmium) are precipitated as the sulphides with ammonium sulphide in the combined ammoniacal filtrates obtained after the separation of iron, arsenic, and other elements, and separated from molybdenum by filtration. Molybdenum is subsequently precipitated as the trisulphide in a tartaric-sulphuric acid medium, and separated from vanadium, tungsten, and residual nickel by filtration. The residual molybdenum in the filtrate is ultimately recovered as the sulphide and the precipitates are combined. After dissolution of the precipitate with nitric and sulphuric acids, and the removal of nitric acid by evaporation with sulphuric acid, the molybdenum in the resulting solution is ultimately determined as described above, after the separation of copper, if present, by reduction with zinc metal.

Wulfenite ores and mill products are decomposed as described above and the solution is evaporated to fumes of sulphur trioxide. Arsenic is reduced to the trivalent state with sulphurous acid, and separated from molybdenum by volatilization as the trichloride. Lead sulphate and acid-insoluble material are ultimately separated by filtration, and the residue is digested in slightly ammoniacal ammonium acetate solution to dissolve the lead sulphate. The remaining residue is ignited, and silica is removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate, and the melt is dissolved in the initial filtrate. Iron, chromium, residual arsenic and other interfering elements are subsequently precipitated as the hydrous oxides and separated from molybdenum as described above. After the addition of tartaric acid to the combined ammoniacal filtrates, some nickel and platinum are separated from molybdenum by an ammonium sulphide separation, and molybdenum is subsequently separated from tungsten, vanadium, and residual nickel by precipitation as the trisulphide and determined as described above.

Discussion of interferences

Iron, chromium, titanium, uranium, vanadium, niobium, and tungsten interfere in the determination of molybdenum because they are also reduced to lower valence states by amalgamated zinc, and subsequently react with either the ferric sulphate employed for the collection of the molybdenum (III), or with the potassium permanganate employed as titrant[3-5]. Copper, nickel, arsenic, antimony, and tin are reduced to the elemental state and contaminate the reductor[4,5]. Nitric acid is reduced to hydroxylamine which is oxidized by the titrant[4]. Organic material causes high results for molybdenum because it is oxidized by the titrant[3].

Interference from iron, chromium, titanium, uranium, niobium, antimony, and tin is eliminated by separating these elements, and various other elements (e.g., zirconium, aluminum, beryllium, bismuth, tantalum, selenium, and tellurium) from molybdenum by precipitation as the hydrous oxides with ammonium hydroxide. Interference from small amounts of arsenic (up to approximately 10 mg) is avoided by separating it by occlusion with hydrous ferric oxide[1-3]. Interference from large amounts of arsenic is eliminated by volatilizing it as the trichloride from a hydrochloric-sulphuric acid medium[3]. Copper is separated from molybdenum by reducing it to the metallic state with zinc metal.

Some nickel and platinum are separated from molybdenum by precipitation as the sulphides with ammonium sulphide. Molybdenum is separated from tungsten, vanadium, and residual nickel by precipitating it as the trisulphide from a dilute sulphuric-tartaric acid medium[1-3].

Lead, which is present in wulfenite ores and mill products, and which interferes because it forms insoluble lead molybdate during the ammonium hydroxide separation of iron, arsenic, and other elements, is separated from molybdenum as lead sulphate prior to the ammonium hydroxide separation step. Lead sulphate is subsequently separated from the molybdenum-bearing acid-insoluble residue by digestion of the residue with ammonium acetate solution[1,3].

Interference from carbonaceous material, introduced from filter paper, is eliminated by oxidizing it with nitric acid and/or potassium permanganate prior to the reduction of molybdenum. Nitric acid is removed by evaporation with sulphuric acid. Platinum, introduced in small amounts from fusions of the acid-insoluble residue in platinum vessels, is reduced to the metallic state in the upper part of the reductor column and does not interfere[4,5].

Range

The method is suitable for samples containing more than approximately 0.5% of molybdenum.

Apparatus

Apparatus for the reduction of molybdenum. Illustrated in Figure 1.

Reagents

Standard potassium permanganate solution, 0.1 N. Prepare as described in the Volumetric-Oxalate Method for calcium (p 242).

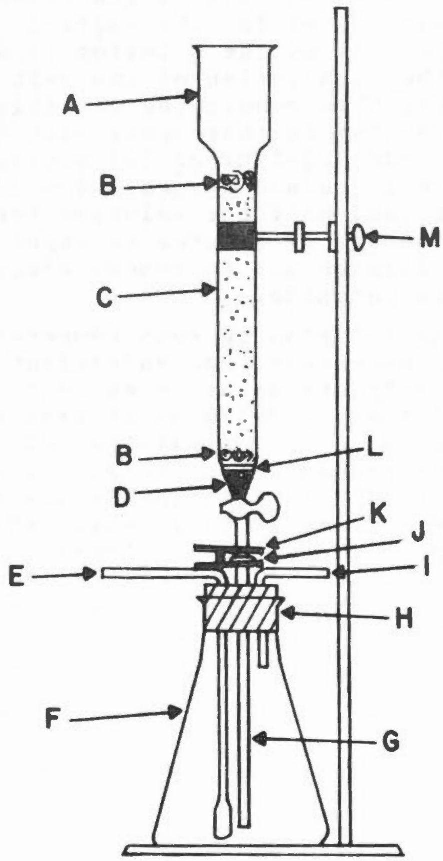

FIGURE 1. Apparatus (Jones reductor) for the reduction of molybdenum

A - Reservoir (approximately 150 ml capacity).
B - Glass-wool.
C - Column of amalgamated zinc (3 x 17 cm).
D - Glass beads.
E - Nitrogen-inlet (gas-dispersion) tube.
F - Titration vessel (1-litre Erlenmeyer flask).
G - Reductor tube.
H - Rubber stopper.
I - Nitrogen-outlet tube.
J - Ball and socket joint.
K - Clamp.
L - Perforated porcelain disc.
M - Clamp.

Reagents (continued)

Amalgamated zinc. Add approximately 800 g of 10-mesh zinc metal (iron content as low as possible) to a 1-litre flask, and add sufficient 8% hydrochloric acid to cover the zinc. Allow the mixture to stand for approximately 1 minute, then pour off the acid (Note 1). Add approximately 400 ml of 2.5% mercuric chloride ($HgCl_2$) solution, shake the mixture for 2-3 minutes, and decant the solution from the zinc. Wash the resulting zinc-mercury amalgam several times, by decantation, with 2% sulphuric acid, then thoroughly with water. Use the washed amalgam to prepare the reductor column (Figure 1) (Notes 2 and 3).

Ferric sulphate solution, 10% w/v. Dissolve 100 g of anhydrous ferric sulphate or an equivalent amount of hydrated reagent, in 1 litre of hot 2% sulphuric acid. Cool the solution, and oxidize any ferrous iron present by adding 2.5% potassium permanganate solution, by drops, until the solution is just slightly pink.

Potassium permanganate solution, 2.5% w/v.

Sulphurous acid solution. Water saturated with sulphur dioxide.

Ammonium hydroxide, 25% and 15% v/v.

Ammonium acetate solution (slightly ammoniacal), 32% w/v. Mix 180 ml of concentrated ammonium hydroxide with 200 ml of water, and add 120 ml of concentrated acetic acid.

Sulphuric acid, 50%, 8%, 6%, 5%, and 2% v/v.

Zinc (20-mesh) granules, high-purity (iron content 0.002% or less).

Hydrogen sulphide (cylinder) gas.

Hydrogen sulphide-tartaric acid wash solution. Dissolve 20 g of tartaric acid in 1 litre of 1% sulphuric acid, and saturate the resulting solution with hydrogen sulphide.

Ammonium acetate wash solution, 5% w/v.

Ammonium sulphide-ammonium tartrate wash solution. Dissolve 10 g of ammonium tartrate in 1 litre of 1% ammonium hydroxide, and saturate the resulting solution with hydrogen sulphide.

Standardization of potassium permanganate solution

Standardize the solution against pure sodium oxalate as described in the Volumetric-Oxalate Method for calcium (p 242). Correct the result obtained by subtracting that obtained for a blank that is carried through the same procedure. Determine the normality of the potassium permanganate solution, and calculate the molybdenum equivalent (mg/ml) (1 ml of 0.1 N potassium permanganate solution = 3.198 mg of molybdenum).

Procedures

A - Molybdenite ores and mill products

(a) Tungsten, nickel, and vanadium absent

Transfer 0.5-4 g of powdered sample, containing up to approximately 300 mg of molybdenum and 150 mg of iron (Note 4), to a 250-ml beaker and, depending on the amount of sample taken, add 10-35 ml of concentrated nitric acid. Add 25 ml of 50% sulphuric acid, cover the beaker, heat gently until the decomposition of the sample or acid-soluble material is complete, then remove the cover and evaporate the solution to dense fumes of sulphur trioxide (Note 5). Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool, add approximately 50 ml of water and boil the solution to dissolve the soluble salts. Filter the resulting solution (Whatman No. 40 paper) into a 250-ml beaker, transfer the residue quantitatively to the filter paper, and wash the paper and residue thoroughly with hot water, then 6-8 times with 5-ml portions of hot 25% ammonium hydroxide followed by hot water.

Transfer the paper and residue (Note 6) to a 30-ml porcelain crucible (Note 7), burn off the paper at a low temperature, and ignite at approximately 400-450°C (Note 8). Cool the crucible, transfer the residue to a 30-ml platinum crucible, and add 1 ml of 50% sulphuric acid and 3-5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess sulphuric acid.

Fuse the residue with 1-2 g of sodium carbonate, cool, and transfer the crucible and contents to the beaker (covered) containing the initial filtrate. Allow the solution to stand until the dissolution of the melt is complete, then remove the crucible after washing it thoroughly with hot water. Add 0.5-1 ml of 30% hydrogen peroxide to reduce any chromium (VI) present, and boil the solution for approximately 10 minutes to expel carbon dioxide and to remove excess hydrogen peroxide.

Cool the solution to room temperature and, if necessary, add sufficient 10% ferric sulphate solution so that approximately 100-150 mg of iron are present (Note 9). Carefully add concentrated ammonium hydroxide, by drops, until the solution is nearly neutral but still clear yellow (Note 10). Heat the solution almost to the boiling point and, while stirring vigorously, slowly pour it into a second 250-ml beaker containing 75 ml of hot (nearly boiling) 15% ammonium hydroxide solution (Note 11). Wash the first beaker with hot water, then with a small amount of hot 15% ammonium hydroxide, and add the washings to the second beaker. Boil the solution for approximately 1 minute, and allow the precipitate to settle. Add a small amount of paper pulp, filter the solution (Whatman No. 540 paper) into an 800-ml beaker, and wash the beaker, paper, and precipitate thoroughly with hot water. Using a jet of hot water, transfer the bulk of the precipitate to the first beaker, add sufficient hot 50% sulphuric acid to dissolve the precipitate, then add 1-2 ml in excess. Add concentrated ammonium hydroxide, by drops, until the solution is nearly neutral, then re-precipitate the hydrous oxides as described above and, using the same filter paper, filter the solution into the beaker containing the initial filtrate. Wash the beaker, paper, and precipitate with hot water. Redissolve the precipitate as described above, repeat the precipitation and filtration procedure, and discard the paper and precipitate.

Neutralize the combined filtrates with concentrated perchloric acid, add 10 ml in excess, and evaporate the solution to approximately 100 ml. Add 60 ml of concentrated nitric acid and

20 ml of concentrated hydrochloric acid, cover the beaker, and heat the solution gently until the vigorous reaction ceases. Remove the cover, evaporate the solution to approximately 50 ml, then add 30 ml of concentrated nitric acid and 10 ml of concentrated hydrochloric acid, cover the beaker, and heat the solution again until the reaction ceases. Remove the cover, wash down the sides of the beaker with water, and evaporate the solution to dryness. Cool, add 13 ml of 50% sulphuric acid and heat gently to dissolve the salts (Note 12). Cool the solution to room temperature, add 2.5% potassium permanganate solution, by drops, until a permanent red tint is obtained, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, evaporate the solution to fumes again to ensure the complete removal of nitric acid, and cool to room temperature.

In the absence of copper, add approximately 100 ml of water and, if necessary, sufficient 50% sulphuric acid so that approximately 6 ml of the concentrated acid are present, and boil the solution for several minutes. Cool the solution to room temperature, and add 2.5% potassium permanganate solution, by drops, until the solution is just slightly pink (Note 13).

Wash the Jones reductor (Figure 1) 5 times with approximately 75-ml portions of warm (40-50°C) 5% sulphuric acid, if it has not been in use for some time. Discard the washings (Notes 14 and 15). Add 35 ml of 10% ferric sulphate solution and 5 ml of concentrated phosphoric acid (Note 16) to the 1-litre Erlenmeyer titration flask F, then add sufficient water so that the tip of the reductor tube G dips well beneath the surface of the solution when the flask is capped with the rubber stopper fitted with the reductor tube. Connect the titration flask to the reductor column, by means of the ball and socket joint J, and bubble nitrogen through the solution for 2-3 minutes to remove dissolved air. Continue the flow of nitrogen (Note 17), and pass the sample solution containing the molybdenum through the reductor (Note 18). Wash the beaker 3 times with 50-ml portions of cold 5% sulphuric acid, and pass the washings through the reductor. Wash the reductor twice with 50-ml portions of water, then close the stopcock while some of the wash water still remains above the zinc (Note 15). Disconnect the reductor at the ball and socket joint, stop the flow of nitrogen, remove the cap of the flask, and wash the inside and outside of the reductor tube and the nitrogen-inlet tube with a small amount of water. Titrate the resulting solution immediately with 0.1 N potassium permanganate solution until a faint pink colour is obtained which persists for approximately 30 seconds (Note 19). Carry a blank, consisting of 100 ml of 6% sulphuric acid, through the reduction procedure, and correct the result obtained for the sample by subtracting that obtained for the blank (Note 20).

In the presence of copper, add approximately 60 ml of water and sufficient 50% sulphuric acid so that approximately 8 ml of the concentrated acid are present (Note 21), and boil the solution for several minutes. Add 2 g of 20-mesh zinc granules, and continue boiling the solution until all of the copper present has been reduced to the metallic state and most of the zinc has dissolved. Filter the solution (Whatman No. 30, 9-cm paper) into a 400-ml beaker, and wash the beaker, paper, and residue with small portions of hot water. Discard the paper and residue. Dilute the filtrate to approximately 100 ml with water and cool to room temperature. Add 2.5% potassium permanganate solution, by drops, until the solution is just slightly pink, then proceed with the reduction and subsequent titration of molybdenum as described above. Carry a blank, prepared by dissolving 2 g of 20-mesh zinc granules in 100 ml of 8% sulphuric acid (Notes 21 and 22), through the reduction procedure, and correct the result obtained for the sample by subtracting that obtained for the blank.

(b) Tungsten, nickel, and/or vanadium present

Following the separation of iron, arsenic, and other elements by precipitation as the hydrous oxides with ammonium hydroxide as described above, add 3 g of tartaric acid (Note 23) to the combined ammoniacal filtrates containing the molybdenum, stir to dissolve and, if necessary, warm the solution. Pass hydrogen sulphide into the solution for 20-30 minutes (Note 24), then filter it (Whatman No. 42 paper) into an 800-ml beaker (Note 25), and wash the paper and precipitate about 15 times with ammonium sulphide-ammonium tartrate wash solution. Discard the paper and precipitate.

Warm the filtrate, cover the beaker and, using litmus paper, carefully neutralize the solution with 50% sulphuric acid. Add 20 ml in excess (Note 26) and heat the solution to the boiling point. Allow the resulting molybdenum trisulphide precipitate to settle, then filter the solution (Whatman No. 42 paper) into a second 800-ml beaker, and wash the paper and precipitate about 15 times with hydrogen sulphide-tartaric acid wash solution. Transfer the paper and precipitate to a 400-ml beaker.

Wash the beaker that contained the precipitate with approximately 20 ml of concentrated nitric acid followed by hot water, add the washings to the filtrate (Note 27), and evaporate the resulting solution to fumes of sulphur trioxide. Cool, add 5-10 ml of concentrated nitric acid, evaporate the solution to fumes again, and continue the nitric acid treatment and subsequent evaporation to fumes until the black or yellow colour due to organic material (i.e., tartaric acid) has disappeared. Cool, add sufficient water to dissolve the salts, then add 2 g of tartaric acid, stir to dissolve, and neutralize the solution approximately with concentrated ammonium hydroxide. Add 5 ml in excess and warm the resulting solution. Saturate the solution with hydrogen sulphide, then neutralize and acidify it with 50% sulphuric acid, as described above, to precipitate the residual molybdenum. Allow the solution to stand for at least 1 hour at 40-60°C, then filter it and wash the precipitate as described above. Discard the filtrate, and transfer the paper and precipitate to the beaker containing the initial precipitate. Wash the beaker that contained the residual molybdenum precipitate with approximately 10 ml of concentrated nitric acid followed by a small amount of hot water. Add the washings to the beaker containing the combined precipitates, and macerate the filter paper thoroughly with a glass rod.

Cover the beaker containing the combined precipitates with a ribbed watch glass, add 10 ml of concentrated sulphuric acid, and cautiously evaporate the solution to dense fumes of sulphur trioxide. Cool, add 10 ml each of water and concentrated nitric acid, evaporate the solution to fumes again, and continue the nitric acid treatment and subsequent evaporation to fumes until the filter paper has been completely destroyed and the yellow colour due to carbonaceous material has disappeared. Cool the solution, remove the cover, and wash down the sides of the beaker with a small amount of water. Add 2.5% potassium permanganate solution, by drops, until a permanent red tint is obtained, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool the solution to room temperature, then, depending on the absence or presence of copper, proceed with the determination of molybdenum as described in Procedure A(a).

B - Wulfenite ores and mill products

Decompose 1-4 g of powdered sample, containing up to approximately 300 mg of molybdenum and 150 mg of iron, as described in Procedure A(a). After evaporation of the solution to fumes of sulphur trioxide, cool the solution, and remove arsenic by volatilization as the trichloride (Note 28) as described in Note 5. Wash down the sides of the beaker with water, and evaporate the solution to fumes of sulphur trioxide to ensure the complete removal of nitric acid. Cool, add approximately 50 ml of water and boil the solution to dissolve the soluble salts. Filter the solution (Whatman No. 40 paper) into a 250-ml beaker, transfer the residue quantitatively to the filter paper, and wash the paper and residue thoroughly with 2% sulphuric acid.

Transfer the paper and residue to a 250-ml beaker, macerate the paper with a glass rod, and add 50 ml of 32% ammonium acetate solution. Digest the mixture just below the boiling point for approximately 5 minutes, then filter the resulting solution (Whatman No. 40 paper) and wash the beaker, paper, and the remaining residue thoroughly with hot 5% ammonium acetate solution. Discard the filtrate.

Transfer the paper and residue to a 30-ml porcelain crucible, burn off the paper at a low temperature, and ignite, decompose, and fuse the resulting residue as described in Procedure A(a). Transfer the crucible and contents to the beaker containing the initial filtrate, allow the solution to stand until the dissolution of the melt is complete, then remove the crucible after washing it thoroughly with hot water. Add 0.5-1 ml of 30% hydrogen peroxide to reduce any chromium (VI) present, and boil the solution for approximately 10 minutes to expel carbon dioxide and to remove excess hydrogen peroxide.

Cool the solution to room temperature, add sufficient 10% ferric sulphate solution, if necessary, so that approximately 100-150 mg of iron are present, and proceed with the ammonium hydroxide separation of iron, arsenic, and other elements as described in Procedure A(a). Add 3 g of tartaric acid to the resulting combined ammoniacal filtrates containing the molybdenum, stir to dissolve, and proceed with the ammonium sulphide separation procedure, the separation of molybdenum as the trisulphide (Note 29), and the subsequent determination of molybdenum as described in Procedure A(b).

Notes

1. The addition of dilute hydrochloric acid to the zinc metal, before the amalgamation procedure, removes some of the "surface" iron present.

2. To prepare the reductor column, fill the reductor with water, add the amalgamated zinc, in small portions, until the tube is filled to the required height, then wash the column with approximately 50 ml of water. When the reductor is not in use it should be kept covered with an inverted beaker and the zinc should be covered with water; this prevents the formation of basic salts which may cause clogging of the column.

3. Care should be taken that no air bubbles are present in the column; this causes low results for molybdenum presumably because of peroxide formation[4].

4. Samples containing more than approximately 150 mg of iron cannot be conveniently handled by this method because of the bulkiness of the iron (III) hydrous oxide precipitate that is obtained during the subsequent ammonium hydroxide separation procedure.

5. If the sample contains more than approximately 10 mg of arsenic, most of it should be removed at this stage (Note 9), by volatilization as the trichloride, as follows[3]:

Cover the beaker, add 20 ml of sulphurous acid solution to reduce the arsenic, and evaporate the solution to approximately 10 ml. Remove the cover, add 10 ml of sulphurous acid solution and 50 ml of concentrated hydrochloric acid, and evaporate the solution to 10-20 ml. Add 10 ml of concentrated nitric acid to re-oxidize the molybdenum, evaporate the solution to dense fumes of sulphur trioxide, then proceed as described.

6. With high-grade molybdenite ores and concentrates, small amounts of acid-insoluble siliceous residue are usually free from molybdenum, after washing with 25% ammonium hydroxide, and can generally be discarded[1]. Large amounts of residue should not be discarded.

7. Residues containing sulphates, sulphides, or other salts of easily reducible elements (e.g., lead, silver, mercury, bismuth, antimony, and tin) should not be ignited in platinum crucibles. These elements may be reduced to the metallic state by the carbon from the filter paper, or by reducing gases from the flame, and will subsequently alloy with and contaminate the crucible.

8. Molybdenum may be lost by volatilization as the trioxide if a higher temperature is employed for ignition.

9. Arsenic (Note 5) is not completely removed by volatilization as the trichloride in the presence of molybdenum[1]. Consequently, to separate any arsenic present in the sample, or remaining after volatilization as the trichloride, sufficient iron (III) must be present in the solution at

this stage to remove the arsenic by occlusion with hydrous ferric oxide during the subsequent ammonium hydroxide separation of iron and other elements. Approximately 100-150 mg of iron (II) (i.e., 4-5 ml of 10% ferric sulphate solution) are sufficient for the separation of up to approximately 10 mg of arsenic[1].

10. The addition of sufficient ammonium hydroxide to impart a permanent amber or red tint to the solution should be avoided[1-3].

11. More molybdenum is retained in the hydrous ferric oxide precipitate if the precipitation of iron is carried out by the usual reverse procedure, in which ammonium hydroxide is slowly added to an acid solution[3].

12. If the solution is amber or deep yellow at this stage the presence of vanadium is indicated. A green colour indicates the presence of copper or nickel. The presence of tungsten is indicated by yellow insoluble hydrated tungsten trioxide. If the solution is green, and nickel, tungsten, and vanadium are known to be absent, remove nitric acid as described, and proceed with the reduction of copper and the subsequent determination of molybdenum as described. If nickel, vanadium, and/or tungsten are present, evaporate the solution to approximately 3 ml, cool, and add about 500 ml of water. Neutralize the solution approximately with concentrated ammonium hydroxide, add 25-30 ml in excess, then add 3 g of tartaric acid, and proceed with the ammonium sulphide separation and the subsequent determination of molybdenum as described in Procedure A(b).

13. The addition of a slight excess of potassium permanganate solution at this stage ensures that any carbonaceous material that may still be present is destroyed before passing the solution through the Jones reductor[3].

14. In normal circumstances, when a series of sample solutions are to be passed through the reductor, 2-3 washes with 75-ml portions of 5% sulphuric acid are sufficient before each subsequent reduction step.

15. To prevent air being drawn through the reductor (Note 3), the level of the liquid in the column should not be allowed to fall below approximately 1 cm above the surface of the zinc during the reduction and washing stages.

16. Phosphoric acid forms a colourless complex with the iron (III) which makes the subsequent end-point easier to detect.

17. A nitrogen atmosphere in the receiving vessel during the reduction stage prevents air-oxidation of the resultant iron (II) and molybdenum (V).

18. The molybdenum solution is green [i.e., molybdenum (III)] as it passes through the lower part of the reductor column, but changes to a bright red [i.e., molybdenum (V)] when it comes into contact with the ferric phosphate (Note 16) in the receiving vessel.

19. The reduced solution can also be titrated with standard potassium dichromate or ceric sulphate solutions, using sodium diphenylaminesulphonate and Ferroin (1,10-phenanthroline ferrous sulphate) as internal indicators, respectively[2,6].

20. The blank compensates for small amounts of iron in the acid solutions passed through the reductor, and in the zinc metal employed in the column. If the zinc is pure, the blank correction should be less than 0.05 ml of 0.1 N potassium permanganate solution[5].

21. Because 2 g of zinc metal react with approximately 2 ml of concentrated sulphuric acid, about 8 ml of concentrated acid should be present at this stage so that the final solution, after removal of the metallic copper by filtration, will be approximately 6% or 1 M in sulphuric acid before passage through the reductor.

22. This blank compensates for any iron present in the zinc metal employed for the reduction of the copper.

23. Tartaric acid prevents tungsten and vanadium from co-precipitating with molybdenum trisulphide in the subsequent procedure when the alkaline

filtrate obtained after the ammonium sulphide separation step is acidified[1].

24. Under these conditions the ammonium hydroxide is converted to ammonium sulphide. The molybdenum remains in solution as ammonium thiomolybdate [$(NH_4)_2MoS_4$] which imparts a deep red colour to the solution[1].

25. Filtration is not necessary if the solution remains clear. Copper, if present, remains entirely in solution at this stage and is coprecipitated as the sulphide with the molybdenum sulphide when the solution is subsequently acidified[1].

26. Under these conditions the ammonium sulphide is converted to ammonium sulphate, the red colour of the ammonium thiomolybdate disappears, and molybdenum is precipitated as the trisulphide, according to the reactions[1]

$$(NH_4)_2S + H_2SO_4 \rightarrow H_2S\uparrow + (NH_4)_2SO_4$$

$$(NH_4)_2MoS_4 + H_2SO_4 \rightarrow MoS_3\downarrow + H_2S\uparrow + (NH_4)_2SO_4.$$

27. Some molybdenum is reduced by hydrogen sulphide in acid solution and passes into the filtrate. This residual molybdenum can be recovered, after re-oxidation to the hexavalent state with nitric acid and the destruction of the tartaric acid, by reprecipitation as the trisulphide as described in the subsequent procedure[3]. Alternatively, if the sample does not contain an appreciable amount of vanadium, tungsten, or coloured ions (i.e., copper and nickel), the residual molybdenum in the filtrate can be determined spectrophotometrically by the Thiocyanate Method, (p 65) as follows:

Following the destruction of the tartaric acid with nitric acid, evaporate the solution to dryness to remove nitric and sulphuric acids. Dissolve the residue in water containing several drops of concentrated hydrochloric acid, transfer the solution to a volumetric flask of appropriate size (100 or 200 ml), and dilute to volume with water. Determine molybdenum in a 5-20-ml aliquot of the resulting solution, and add the percentage obtained to the result obtained after the destruction of the paper and precipitate containing the molybdenum trisulphide precipitate as described in the subsequent procedure.

28. Preliminary removal of arsenic is recommended because wulfenite ores and concentrates often contain several percent of mimetite (lead chloroarsenate)[1,3].

29. The separation of molybdenum as the trisulphide is generally necessary with wulfenite ores and mill products because wulfenite ores usually contain tungsten[1].

Calculations

Molybdenum equivalent (mg/ml) of the potassium permanganate solution (Mo_{EQ})

$$= N \times \frac{1}{3} \times 95.94$$

where:

N = normality of the potassium permanganate solution.

$$\% \text{ Mo} = \frac{(V_S - V_B) \times Mo_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium permanganate solution required by the sample.

V_B = volume (ml) of potassium permanganate solution required by the blank.

$\% \text{ MoS}_2 = 1.669 \times \% \text{ Mo}$

$\% \text{ MoO}_3 = 1.500 \times \% \text{ Mo}$

Other applications

This method can be employed to determine molybdenum in ferro-molybdenum[7].

References

1. W.W. Scott and N.H. Furman, "Standard Methods of Chemical Analysis", 5th ed., The Technical Press Ltd., London, vol. 1, pp 594-601 (1939).

2. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 689-692 (1962).

3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 302-309 (1953).

4. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc., New York, vol. III, pp 11-14 (1957).

5. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, 599 (1948).

6. J. Belcher and C.J. Coetzee, Analyst, 92, 166 (1967).

7. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E 31, pp 104-106 (1971).

DETERMINATION OF PHOSPHORUS IN MANGANESE, IRON, MOLYBDENUM AND TUNGSTEN ORES AND MILL PRODUCTS, PHOSPHATE ROCK, LIMESTONE, CLAY, SHALE, ACID-SOLUBLE AND REFRACTORY SILICATE ROCKS AND MINERALS, AND BAUXITE BY THE ALKALIMETRIC METHOD AFTER PRECIPITATION AS AMMONIUM PHOSPHOMOLYBDATE

Principle

This method[1,2] involves the precipitation of orthophosphate as ammonium phosphomolybdate from a 2 M nitric acid-ammonium nitrate medium, and the subsequent dissolution of the yellow precipitate in a measured excess of standard sodium hydroxide solution. Phosphorus is determined from the amount of sodium hydroxide solution required to react with the precipitate, after back-titration of the excess alkali with standard nitric acid, in the presence of phenolphthalein as internal indicator.

The corresponding reactions for these processes are:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 \rightarrow (NH_4)_3PO_4\cdot 12MoO_3\cdot 2HNO_3\cdot H_2O + 21NH_4NO_3 + 12H_2O$$

$$(NH_4)_3PO_4\cdot 12MoO_3 + 23NaOH \rightarrow 11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O.$$

Outline

Manganese and iron ores and mill products, containing up to approximately 15 mg of titanium, are decomposed with hydrochloric acid. The solution is treated with nitric acid to convert phosphorus to orthophosphate, and silica is dehydrated by evaporation with perchloric acid. The acid-insoluble material is ultimately removed by filtration and ignited. Silica is subsequently removed by volatilization as silicon tetrafluoride. The resultant residue is fused with sodium carbonate to convert refractory phosphates (titanium, zirconium, and possibly thorium) to soluble sodium phosphate. The melt is digested in water, and the hydrous oxides of the above elements are removed by filtration. The residual phosphorus in the filtrate is subsequently co-precipitated as ferric phosphate with hydrous ferric oxide. After dissolution of the precipitate, the resultant solution is added to the initial filtrate, and the phosphorus in the combined solution is ultimately precipitated as ammonium phosphomolybdate with ammonium molybdate, and separated by filtration. The precipitate is dissolved in sodium hydroxide solution, and the excess sodium hydroxide in the resulting solution is titrated with dilute nitric acid.

> Samples containing more than 15 mg of titanium are decomposed by fusion with sodium carbonate and sodium nitrate. The melt is digested in water, and the hydrous oxides of titanium, zirconium, thorium, and various other elements are removed by filtration. The phosphorus in the filtrate is subsequently co-precipitated as ferric phosphate with hydrous ferric oxide, and the precipitate is dissolved in dilute hydrochloric acid. After dehydration of the residual silica, and its removal by filtration, the phosphorus in the resulting filtrate is ultimately precipitated with ammonium molybdate and determined as described above.

Molybdenum and tungsten ores and mill products are decomposed with hydrochloric, nitric, and sulphuric acids, and the solution is evaporated to fumes of sulphur trioxide to dehydrate silica. The acid-insoluble material is removed by filtration, and ignited, decomposed, and fused as described above. The melt is dissolved in dilute hydrochloric acid, and the solution is added to the initial filtrate. Molybdenum and tungsten are ultimately complexed with tartaric acid, and phosphorus is precipitated as magnesium ammonium phosphate with magnesium sulphate from an ammoniacal medium, and separated from molybdenum, tungsten, and other interfering elements by filtration. After dissolution of the precipitate, the phosphorus in the resulting solution is ultimately precipitated with ammonium molybdate and determined as described above.

Phosphate rock and limestone are decomposed by the acid-decomposition procedure described for manganese and iron ores, and the acid-insoluble material is treated in a similar manner. The phosphorus in the subsequent combined phosphate rock solution is determined in an aliquot of the solution after precipitation as ammonium phosphomolybdate. The phosphorus in the combined limestone solution is determined as described in the fusion procedure for manganese and iron ores, after its separation by co-precipitation with hydrous ferric oxide, and dissolution of the precipitate in dilute hydrochloric acid.

Refractory silicate rocks and minerals, and clay, shale, bauxite, and acid-soluble silicate rocks and minerals containing more than 15 mg of titanium are decomposed and analyzed as described in the fusion procedure for manganese and iron ores. Clay, shale, bauxite, and acid-soluble silicate rocks and minerals containing 15 mg or less of titanium are decomposed with nitric, hydrofluoric, and perchloric acids. The solution is evaporated to fumes of perchloric acid to remove silica and hydrofluoric acid, and phosphorus is ultimately separated by co-precipitation with hydrous ferric oxide, and determined as described in the acid-decomposition procedure for manganese and iron ores.

Discussion of interferences

Titanium, zirconium, bismuth, thorium, and tin interfere in the precipitation of phosphorus as ammonium phosphomolybdate by forming insoluble phosphates. Tungsten (VI) and vanadium (V) retard precipitation and/or contaminate the precipitate because they form heteropoly compounds with phosphorus. Arsenic, germanium, silicon, selenium, and tellurium interfere in a similar manner because they form similar heteropoly compounds with ammonium molybdate[3-5]. Hydrochloric and hydrofluoric acids, employed for sample decomposition, also retard the precipitation of phosphorus[3-5]; these are removed during sample decomposition, or before precipitation, by evaporation with perchloric acid.

Interference from arsenic, germanium, and tin can be avoided by volatilizing these elements as the bromides from a hydrobromic-perchloric or a hydrobromic-sulphuric acid medium. Silica is volatilized as silicon tetrafluoride by treatment of the sample or the acid-insoluble residue with hydrofluoric and perchloric acids. Titanium, zirconium, thorium, some bismuth, and various other elements (e.g., iron, nickel, cobalt, copper, cadmium, manganese, niobium, tantalum, and the alkaline earths) are separated from phosphorus (either in the sample or in the acid-insoluble residue) by filtration of their hydrous oxides, after fusion of the sample or acid-insoluble residue with sodium carbonate and subsequent digestion of the melt in water[3,6].

Phosphorus is separated from large amounts of sodium salts, introduced during the sodium carbonate fusion, and from copper, nickel, and chromium (VI), which may interfere if present in appreciable amounts, by co-precipitating it as ferric phosphate with hydrous ferric oxide from an ammoniacal ammonium chloride medium[3].

Interference from large amounts of tungsten and molybdenum, and from other elements that may be present in tungsten and molybdenum ores (e.g., tin, titanium, vanadium, chromium, bismuth, selenium, tellurium, and zirconium) is eliminated by separating phosphorus from these elements by precipitation as magnesium ammonium phosphate from an ammoniacal tartrate medium[3,7,8]. Interference from vanadium (V), during the precipitation of phosphorus as ammonium phosphomolybdate, is avoided by reducing it to the tetravalent state with iron (II); vanadium (IV) does not interfere if phosphorus is precipitated at 10-20°C[3].

Lead interferes in this method because it forms insoluble lead molybdate which reacts with the sodium hydroxide solution employed for the dissolution of the ammonium phosphomolybdate precipitate[5]. Bismuth, selenium, and tellurium interfere in all of the procedures described except that in which phosphorus is first separated as magnesium ammonium phosphate.

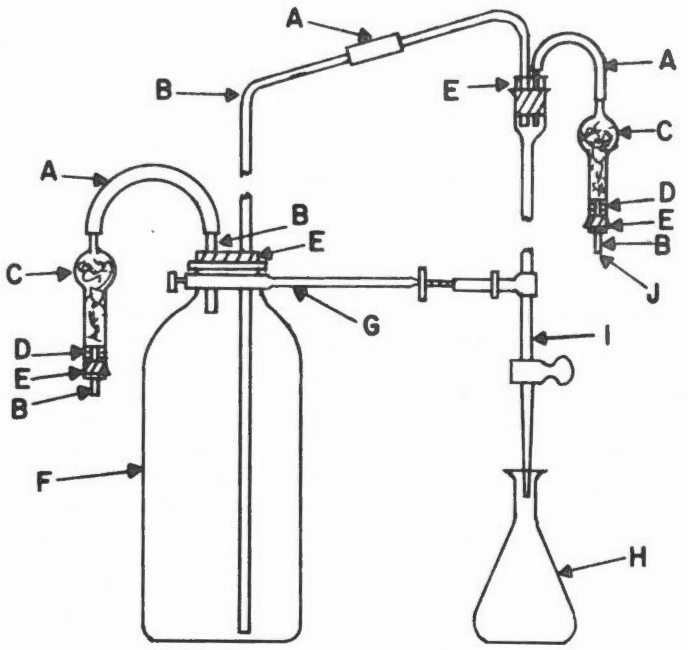

FIGURE 1. Apparatus for the protection of the standard sodium hydroxide solution against carbon dioxide

A - Plastic (Tygon) tubing.
B - Glass tubing.
C - Drying tube filled with Ascarite.
D - Glass-wool.
E - Rubber stopper.
F - Polyethylene bottle containing standard sodium hydroxide solution.
G - Clamp.
H - Titration vessel (300-ml).
I - Burette (50-ml).
J - Connection for suction.

Range

The method is suitable for ores and mill products containing approximately 0.02 to 4% of phosphorus, and for various other materials containing more than approximately 0.01% of phosphorus.

Apparatus

Apparatus for the protection of the standard sodium hydroxide solution against carbon dioxide. Illustrated in Figure 1.

Shaking machine.

Reagents

Sodium hydroxide stock solution, 30% w/v. Dissolve 300 g of sodium hydroxide in 1 litre of water, and add a slight excess of barium hydroxide to precipitate any carbon dioxide present (Note 1). Allow the precipitate to settle, then store the solution in a polyethylene bottle.

Standard sodium hydroxide solution, 0.15 N. Dilute 40 ml of the clear, supernatant stock solution to 2 litres with carbon dioxide-free water. Store the solution in a polyethylene bottle and protect it from atmospheric carbon dioxide by means of drying tubes filled with Ascarite (asbestos impregnated with sodium hydroxide) as shown in Figure 1.

Standard nitric acid, 0.15 N. Dilute 20 ml of concentrated, colourless nitric acid to 2 litres with water.

Phenolphthalein indicator solution, 0.2% w/v in ethyl alcohol. Store in a dropping bottle.

Ammonium molybdate solution. Transfer 100 g of molybdic acid (85% molybdenum trioxide) to a 600-ml beaker containing 240 ml of water, mix thoroughly and, while stirring, add 140 ml of concentrated ammonium hydroxide. When dissolution of the molybdic acid is complete, filter the solution (Whatman No. 30 paper), add 60 ml of concentrated nitric acid, and cool the solution to room temperature. Add 400 ml of concentrated nitric acid to 960 ml of water in a separate 2-litre beaker, and cool the solution to room temperature. While stirring, combine the two solutions, add 0.1 g of dibasic ammonium orthophosphate [$(NH_4)_2HPO_4$] (Note 2), and allow the resulting solution to stand for at least 24 hours. Use only the clear supernatant liquid, or filter the solution before use.

Magnesium sulphate solution, 40% w/v. Dissolve 40 g of magnesium sulphate heptahydrate ($MgSO_4 \cdot 7H_2O$) in water and dilute to 100 ml.

Iron (III) solution, 3% w/v. Dissolve 15 g of high-purity iron metal (phosphorus-free) in 100 ml of concentrated hydrochloric acid, add several drops of concentrated nitric acid to oxidize any ferrous iron present, cool, and dilute the solution to 500 ml with water.

Ferrous sulphate solution, 10% w/v. Dissolve 10 g of ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) in 100 ml of 5% sulphuric acid. Prepare fresh as required.

Hydrogen peroxide, 3% w/v. Dilute 10 ml of 30% hydrogen peroxide to 100 ml with water.

Nitric acid, 25% v/v.

Ammonium hydroxide, 50% and 5% v/v.

Hydrochloric acid, 50% v/v.

Sulphuric acid, 50% v/v.

Nitric acid wash solution (carbon dioxide-free), 1% v/v. Prepare with carbon dioxide-free water.

Potassium nitrate wash solution (carbon dioxide-free), 1% w/v. Prepare with carbon dioxide-free water.

Sodium carbonate wash solution, 2% w/v.

Sodium carbonate-sodium nitrate fusion mixture, 90% and 10% by weight, respectively.

Water (carbon dioxide-free). Freshly boiled and cooled water.

Standardization of sodium hydroxide solution

Transfer 1.0000 g of pure potassium acid phthalate (dried at 120°C for 1-2 hours) to a 300-ml Erlenmeyer flask that has been purged of carbon dioxide with nitrogen. Add 50 ml of carbon dioxide-free water, stopper, and shake gently until the phthalate has dissolved. Add 3 drops of 0.2% phenolphthalein solution, and titrate the resulting solution with standard sodium hydroxide solution to a faint pink end-point (Note 3). Determine the normality of the sodium hydroxide solution, and calculate the phosphorus equivalent (mg/ml) (1 ml of 0.15 N sodium hydroxide solution = 0.2021 mg of phosphorus).

Alternatively, the sodium hydroxide solution can be standardized against a sample of iron ore or phosphate rock of known phosphorus content, by carrying the sample through the described procedure, and the phosphorus equivalent can be determined by direct calculation.

Standardization of nitric acid solution

Transfer a 25-40-ml aliquot of the standard sodium hydroxide solution to a 300-ml Erlenmeyer flask, and dilute to approximately 50 ml with carbon dioxide-free water. Add 3 drops of 0.2% phenolphthalein solution, and titrate the resulting solution with standard nitric acid to a colourless end-point. Determine the normality of the nitric acid solution, and calculate the sodium hydroxide equivalent (ml/ml) (1 ml of 0.15 N nitric acid = 1 ml of 0.15 N sodium hydroxide solution) (Note 4).

Procedures

In these procedures a reagent blank is carried along with the samples.

A - Manganese and iron ores and mill products

(a) Titanium content 15 mg or less

Transfer 0.2-1 g of powdered sample, containing up to approximately 7.5 mg of phosphorus, to a 400-ml beaker, moisten with several ml of water, and add 25 ml of concentrated hydrochloric acid. Cover the beaker, and heat gently, without boiling, until the decomposition of acid-soluble material is complete. Add 5 ml of concentrated nitric acid and 20 ml of concentrated perchloric acid, evaporate the solution to fumes of perchloric acid, and continue fuming for 5-10 minutes to dehydrate the silica. Cool, add 50 ml of water and heat gently to dissolve the soluble salts (Note 5). Filter the resulting solution (Whatman No. 40 paper) into a 300-ml Erlenmeyer flask, transfer the residue quantitatively to the filter paper, and wash the paper and residue 3-5 times with 1% nitric acid, then thoroughly with hot water to remove perchlorates. Evaporate the filtrate and washings to approximately 25 ml.

Transfer the paper and residue to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 750°C. Cool the crucible and add 2 ml of concentrated perchloric acid and 5 ml of concentrated hydrofluoric acid. Heat gently to decompose the residue, then evaporate the solution to dryness to remove silica and excess perchloric acid. Fuse the residue with 1-3 g of sodium carbonate, cool, and transfer the crucible and contents to a 250-ml beaker. Add 100 ml of water, heat gently to disintegrate the melt and to dissolve the soluble salts, then remove the crucible after washing it thoroughly with hot water. Filter the resulting solution (Whatman No. 40 paper) into a 400-ml beaker, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue (Note 6).

Add 10 ml of concentrated hydrochloric acid to the filtrate, boil the solution for several minutes to expel carbon dioxide, cool and add 1 ml of 3% iron (III) solution. Neutralize the solution approximately with concentrated ammonium hydroxide to precipitate the hydrous oxide of iron and ferric phosphate, add 1-2 ml in excess, and boil the resulting solution for approximately 1 minute to coagulate the precipitate. Filter the solution (Whatman No. 541 paper), wash the beaker, paper, and precipitate several times with hot water, and discard the filtrate. Dissolve the precipitate, using 10 ml of warm 50% hydrochloric acid, and wash the paper thoroughly with hot water. Collect the solution in the beaker in which the precipitation was carried out, and discard the paper. Add the solution to the initial filtrate (Note 7) and evaporate the combined solution to fumes of perchloric acid. Cool, add 50 ml of water and heat gently to dissolve the salts (Notes 5 and 8).

Add concentrated ammonium hydroxide to the resulting solution until a small precipitate of hydrous ferric oxide is formed which persists on shaking or stirring. Add concentrated nitric acid, by drops, until the precipitate just dissolves, then add 3-5 ml in excess. Add 10 g of ammonium nitrate (Note 9), shake to dissolve, and dilute the solution to approximately 100 ml with water. Cool the solution to 15°C (Note 10) in an ice-bath, add 5 ml of 10% ferrous sulphate solution, swirl the flask to reduce vanadium (Note 11), and add 60 ml of ammonium molybdate solution. Stopper, and shake the flask vigorously in a shaking machine for at least 10 minutes, then allow the solution to stand for 1 hour, or until the yellow ammonium phosphomolybdate precipitate has settled (Note 12). Filter the solution, using a smooth funnel containing a pad of macerated paper pulp (Whatman No. 40) supported on a perforated disc. Wash the flask 3 times and the precipitate 5 times with 5-ml portions of 1% carbon dioxide-free nitric acid (Note 13), then wash the flask and precipitate with 1% carbon dioxide-free potassium nitrate solution until the washings are free of acid, as indicated by a test with litmus paper (Notes 14 and 15).

Transfer the disk, paper pulp pad, and the precipitate to the Erlenmeyer flask in which the precipitation was carried out (Note 16). Add 25 ml of carbon dioxide-free water, and sufficient 0.15 N sodium hydroxide solution to decompose the precipitate and to provide approximately a 5-ml excess. Stopper, and shake until the precipitate has dissolved.

Wash down the sides of the flask with carbon dioxide-free water, add 3 drops of 0.2% phenolphthalein solution, and titrate the excess sodium hydroxide solution with 0.15 N nitric acid to a colourless end-point. Determine the volume of sodium hydroxide solution required by the sample, and correct the result obtained by subtracting that obtained for the reagent blank.

(b) Titanium content more than 15 mg

Transfer 0.2-1 g of sample to a 30-ml platinum crucible lined with fused sodium carbonate, add a ten-fold weight excess of 90% sodium carbonate-10% sodium nitrate fusion mixture and mix thoroughly. Cover the crucible, fuse the mixture over a blast burner, and keep the melt at red heat for several minutes to ensure complete sample decomposition. Cool, transfer the crucible and cover to a 400-ml beaker, and add approximately 100 ml of water. Heat gently to disintegrate the melt, then remove the crucible and cover after washing them thoroughly with hot water. Boil the solution for several minutes to dissolve the soluble salts, filter it (Whatman No. 540 paper) into a 600-ml beaker, and wash the beaker, paper, and precipitate thoroughly with 2% sodium carbonate solution. Discard the paper and precipitate.

Add 10 ml of concentrated hydrochloric acid to the filtrate, and boil the solution for several minutes to expel carbon dioxide. Add 4 ml of 3% iron (III) solution, then proceed with the precipitation, filtration, and washing of hydrous ferric oxide and ferric phosphate as described in Procedure A(a). Dissolve the precipitate, using 20 ml of warm 50% hydrochloric acid, and wash the paper thoroughly with hot water. Collect the resulting solution in a 250-ml beaker, and discard the paper. Wash the beaker that contained the precipitate with a small amount of 50% hydrochloric acid followed by hot water, and add the washings to the main solution.

Add 10-15 ml of concentrated perchloric acid (Note 7) to the resulting solution, evaporate it to fumes of perchloric acid, cover the beaker, and continue fuming for 5-10 minutes to dehydrate any silica present. Cool, add 50 ml of water and heat gently to dissolve the salts (Note 5). If necessary, filter the solution (Whatman No. 541 paper) into a 300-ml Erlenmeyer flask, and wash the beaker, paper, and residue with warm 1% nitric acid. Discard the paper and residue (Note 8), and evaporate the filtrate and washings to approximately 50 ml. Neutralize the solution approximately with concentrated ammonium hydroxide, add 3-5 ml of concentrated nitric acid and 10 g of ammonium nitrate, then proceed with the precipitation of ammonium phosphomolybdate (Note 11) and the subsequent determination of phosphorus as described above.

B - Molybdenum and tungsten ores and mill products

Transfer 0.2-1 g of powdered sample, containing up to approximately 7.5 mg of phosphorus, to a 400-ml beaker, and moisten with several ml of water. Add 20 ml of concentrated nitric acid, cover the beaker, and boil gently until the decomposition of sulphide minerals appears to be complete. Add 20 ml of concentrated hydrochloric acid and 20 ml of 50% sulphuric acid, and gently (Note 17) evaporate the solution to fumes of sulphur trioxide to dehydrate silica (Note 18). Cool, add 50 ml of water and heat gently to dissolve the soluble salts. Filter the resulting solution (Whatman No. 40 paper) into a 300-ml Erlenmeyer flask, transfer the residue quantitatively to the filter paper, and wash the paper and residue (Note 19) thoroughly with hot water, then with 5-10 ml of 50% ammonium hydroxide followed by hot water. Evaporate the filtrate and washings to approximately 25 ml.

Transfer the paper and residue to a 30-ml platinum crucible, and ignite, decompose, and fuse the residue as described in Procedure A(a). Transfer the crucible and contents to the original beaker, add approximately 50 ml of water, cover the beaker, and dissolve the melt by adding 6 ml of concentrated hydrochloric acid in small portions. Remove the crucible after washing it thoroughly with hot water, cover the beaker, and boil the solution to expel carbon dioxide. Add the resulting solution to the initial filtrate (Note 20), and evaporate the combined solution to fumes of sulphur trioxide. Cool, add 50 ml of water and heat gently to dissolve the salts (Note 21).

Add 2 g of tartaric acid (Note 22), stir to dissolve, then cool the solution to approximately 50°C, and add 40 ml of 50% ammonium hydroxide (Note 23). While the solution is still hot from the reaction between sulphuric acid and ammonium hydroxide, add 10 ml of 40% magnesium sulphate solution, then cool the solution to 5-10°C in an ice-bath, add 4 or 5 glass beads (approximately 6 mm in diameter) (Note 24) and stopper the flask tightly. Shake the flask vigorously in a shaking machine for at least 10 minutes, then add 15 ml of concentrated ammonium hydroxide, place the flask in a refrigerator, and allow the solution to stand overnight (Note 25) to complete the precipitation of magnesium ammonium phosphate. Filter the resulting solution through a 9-cm Whatman No. 40 paper containing a small amount of ashless paper pulp, and wash the flask, paper, and precipitate thoroughly with small portions of 5% ammonium hydroxide (Note 26).

Place the Erlenmeyer flask that contained the precipitate under the funnel, and dissolve the precipitate with approximately 40 ml of 25% nitric acid. Wash the paper, including the inside flap, thoroughly with hot water, and discard the paper. Wash down the sides of the flask with a small amount of 25% nitric acid (Note 27) and neutralize the resulting solution approximately with concentrated ammonium hydroxide. Add 3-5 ml of concentrated nitric acid and 2 g of ammonium nitrate (Note 28) and stir to dissolve. Cool the solution to approximately 20-25°C, add 60 ml of ammonium molybdate solution, then proceed with the precipitation of ammonium phosphomolybdate and the subsequent determination of phosphorus as described in Procedure A(a).

C - Phosphate rock

Transfer 1 g of powdered sample to a 250-ml beaker, add approximately 10 ml of water, 5 ml each of concentrated nitric and hydrochloric acids, and 20 ml of concentrated perchloric acid. Cover the beaker, evaporate the solution to fumes of perchloric acid, and continue fuming for 5-10 minutes to dehydrate silica. Cool, add 50 ml of water and heat gently to dissolve the soluble salts. Filter the resulting solution (Whatman No. 40 paper) into a 400-ml beaker, and transfer the residue quantitatively to the filter paper. Wash the paper and residue with 1% nitric acid followed by hot water to remove perchlorates, then ignite, decompose, and fuse the residue, and digest the melt in water as described in Procedure A(a). Filter the resulting solution into the beaker containing the initial filtrate, and wash the beaker, paper, and residue thoroughly with hot water. Discard the paper and residue, and boil the solution for several minutes to expel carbon dioxide (Note 7).

Cool the solution to room temperature, transfer it to a 500-ml volumetric flask, dilute to volume with water and mix. Transfer a 20-25-ml aliquot, containing up to 7.5 mg of phosphorus, to a 300-ml Erlenmeyer flask, and evaporate to fumes of perchloric acid. Cool, add 50 ml of water and heat gently to dissolve the salts (Note 8). Neutralize the solution approximately with concentrated ammonium hydroxide, add 3-5 ml of concentrated nitric acid and 10 g of ammonium nitrate, then proceed with the precipitation and determination of phosphorus as described in Procedure A(a).

D - Limestone

Decompose 0.5-2 g of powdered sample by the method described in Procedure C, using 10 ml of concentrated perchloric acid rather than 20 ml (Note 29). Filter the resulting solution and treat the residue as described in Procedure A(a), then filter the solution of the sodium carbonate melt into the beaker containing the initial filtrate. Wash the beaker, paper, and residue thoroughly with hot water, and discard the paper and residue. Boil the combined solution for several minutes to expel carbon dioxide, then add 10 ml of concentrated hydrochloric acid and 4 ml of 3% iron (III) solution. Dilute the solution to approximately 200 ml with water, and proceed with the precipitation and filtration of hydrous ferric oxide and ferric phosphate, and the subsequent precipitation and determination of phosphorus as described in Procedure A(b).

E - Clay, shale, bauxite, and acid-soluble silicate rocks and minerals containing 15 mg or less of titanium

Transfer 0.5-2 g of powdered sample to a 100-ml platinum dish, and moisten with approximately 5 ml of water. Add 5 ml of concentrated nitric acid and 10 ml each of concentrated hydrofluoric and perchloric acids, and evaporate the solution to fumes of perchloric acid. Cool, add 10 ml each of water and concentrated hydrofluoric acid, evaporate the solution to fumes again and, if necessary, repeat the addition of water and hydrofluoric acid and the subsequent evaporation to fumes until the decomposition of the sample is complete. Cool, wash down the sides of the dish with water, and evaporate the solution to fumes again to ensure the complete removal of hydrofluoric acid. Cool, add 30 ml of water and heat gently to dissolve the salts. If necessary (Note 30), filter the solution into a 400-ml beaker, and wash the dish and paper thoroughly with 1% nitric acid and hot water (Note 7).

Add 10 ml of concentrated hydrochloric acid and 4 ml of 3% iron (III) solution (Note 31), dilute the solution to approximately 200 ml with water, and proceed with the precipitation and filtration of hydrous ferric oxide and ferric phosphate as described in Procedure A(b). Dissolve the precipitate, using 40 ml of 25% nitric acid, and wash the paper thoroughly with hot water. Collect the solution in a 300-ml Erlenmeyer flask, and discard the paper. Wash the beaker that contained the precipitate with a small amount of 25% nitric acid followed by hot water, and add the washings to the main solution. Neutralize the resulting solution approximately with concentrated ammonium hydroxide, add 3-5 ml of concentrated nitric acid and 2 g of ammonium nitrate (Note 28), and proceed with the precipitation and determination of phosphorus as described in Procedure A(a).

F - Refractory silicate rocks and minerals, and clay, shale, bauxite, and acid-soluble silicate rocks and minerals containing 15 mg or more of titanium

Decompose 0.5-2 g of powdered sample and determine phosphorus by the method described in Procedure A(b).

Notes

1. All glassware should be cleaned with hot concentrated hydrochloric acid, and then washed with water to remove any phosphorus-bearing compounds.

2. Dibasic ammonium orthophosphate is added to saturate the solution with ammonium phosphomolybdate. During analysis this reduces the loss of phosphorus due to the solubility of the precipitate.

3. A 1.0000-g portion of potassium acid phthalate requires 32.64 ml of 0.15 N sodium hydroxide solution.

4. For convenience, the standard nitric acid can be made equivalent to the standard sodium hydroxide solution by the addition of more concentrated nitric acid, or by appropriate dilution with water as required. If more nitric acid is required, the volume to be added can be calculated as follows:

$$\text{Volume (ml) of concentrated nitric acid required} = \frac{V \times (D_N - A_N)}{N_{HNO_3}}$$

where:

V = *volume (ml) of stock solution remaining.*

D_N = *desired normality.*

A_N = *actual normality.*

N_{HNO_3} = *normality of concentrated nitric acid.*

If dilution is required, the volume of the solution after dilution, and subsequently the amount of water to be added, can be calculated as follows:

$$\text{Volume (ml) after dilution } (V_{AD}) = \frac{A_N \times V}{D_N}$$

where:

A_N, V and D_N are *as described above*.
Then, volume (ml) of water to be added $= V_{AD} - V$.

After adjustment of the normality by either method the solution should be checked by further titration against the standard sodium hydroxide solution.

5. If the sample contains an appreciable amount of manganese, any manganese dioxide that may have precipitated during evaporation of the solution to fumes of perchloric acid may be re-dissolved by the addition of several drops of 3% hydrogen peroxide. The solution should subsequently be boiled for approximately 5 minutes to remove excess hydrogen peroxide.

6. Filtration of the aqueous solution of the sodium carbonate melt removes the titanium that was present in the acid-insoluble residue, but most of the titanium that is present in the sample remains in the initial filtrate. Small amounts do not interfere appreciably during the precipitation of phosphorus as ammonium phosphomolybdate[3], but prior separation of titanium, as described in Procedure A(b), is necessary for samples containing more than approximately 15 mg[2].

7. If the sample contains arsenic, tin, or germanium proceed as follows:

Evaporate the solution to approximately 30 ml, add 5-10 ml of concentrated hydrobromic acid, and evaporate the solution to fumes of perchloric acid. Cool, wash down the sides of the flask with water, evaporate the solution to fumes again, then proceed as described.

Antimony is also volatilized as the bromide by the above procedure.

8. If a small amount of insoluble silica is present, filter the solution (Whatman No. 541 paper) into a 300-ml Erlenmeyer flask and wash the paper and residue with warm 1% nitric acid. Discard the paper and residue, and evaporate the filtrate and washings to approximately 50 ml, then proceed as described.

If a large amount is present, ignite the paper and residue, and treat the resulting residue as described in Procedure A(a). After digestion of the sodium carbonate melt, filter the solution, and add the filtrate to the main solution.

9. Ammonium nitrate hastens the separation of the ammonium phosphomolybdate precipitate, and decreases its solubility because of the common-ion effect[4].

10. Precipitation of phosphorus at 15°C eliminates interference from vanadium (IV). Tetravalent vanadium retards precipitation, to some extent, but it is not occluded by the precipitate if phosphorus is precipitated at 10-20°C[3].

11. If vanadium is absent, cool the solution to approximately 20°C, omit the addition of ferrous sulphate solution, and allow the solution to stand for 20 minutes after it is removed from the shaking machine, or until the yellow precipitate has settled[1].

12. If the amount of precipitate is small, the solution should be allowed to stand for at least 4 hours or preferably overnight[1,3].

13. Because the yellow precipitate tends to climb up the sides of the funnel, wash it by directing a jet of the wash solution around the inner edge of the funnel and spirally down. It is not necessary to remove all of the precipitate from the flask.

14. Because sodium hydroxide reacts with nitric acid and carbon dioxide, high results will be obtained if potassium nitrate solution containing carbon dioxide is employed as wash solution, and if all of the acid is not removed from the flask and precipitate.

15. When only a few determinations are required, phosphorus can be determined gravimetrically at this stage by collecting the precipitate quantitatively in a tared porcelain filtering crucible, and washing it with 1% nitric acid. Subsequently, the precipitate can be weighed as ammonium phosphomolybdate $[(NH_4)_3PO_4 \cdot 12MoO_3]$, after drying it to constant weight at 110-115°C, or as phosphomolybdic anhydride $(P_2O_5 \cdot 24MoO_3)$, after igniting it at approximately 400°C.

Then, %P =

$$\frac{0.01651 \times \text{Weight of dried ammonium phosphomolybdate (g)}}{\text{Sample weight (g)}} \times 100$$

OR

$$= \frac{0.01722 \times \text{Weight of ignited phosphomolybdic anhydride (g)}}{\text{Sample weight (g)}} \times 100$$

The latter method is more accurate than the preceding method because all ammonium salts are expelled, and possible error resulting from variations in the composition of the ammonium phosphomolybdate precipitate because of occluded ammonium salts is eliminated[4].

16. Any precipitate adhering to the glass funnel can be removed by first washing the funnel with a small amount of carbon dioxide-free water, then by wiping it with a moistened piece of filter paper.

17. Rapid evaporation and strong fuming at high temperatures result in spattering and possible loss of phosphorus by volatilization[4], and cause hard crusts, that resist subsequent treatment, to form on the bottom of the beaker.

18. If the sample is a molybdenite concentrate, more nitric acid, followed by evaporation of the solution to fumes of sulphur trioxide, may be required to decompose any remaining sulphides.

19. If the sample contains an appreciable amount of tungsten, insoluble yellow hydrated tungsten trioxide will constitute most of the acid-insoluble material after filtration. This compound is re-dissolved into the filtrate by the subsequent treatment with 50% ammonium hydroxide. The ammonium hydroxide employed should be kept to a minimum so that the filtrate will remain acid.

20. If the sample contains arsenic, tin, or germanium proceed as follows:

Evaporate the solution to approximately 30 ml, add 5-10 ml of concentrated hydrobromic acid, and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the flask with water, evaporate the solution to fumes again, then proceed as described.

21. Insoluble hydrated tungsten trioxide may be present at this stage.

22. The amount of tartaric acid employed should not exceed 2 g because the ammonium tartrate that is subsequently produced retards the formation of magnesium ammonium phosphate (Note 25)[8].

23. If a large amount of hydrated tungsten trioxide is present, more ammonium hydroxide and gentle heating may be required to dissolve this compound and produce a clear solution.

24. Glass beads initiate the formation of the magnesium ammonium phosphate precipitate.

25. In the presence of ammonium tartrate, complete precipitation of phosphorus as magnesium ammonium phosphate can be obtained only by vigorous agitation of a very cold solution, followed by long standing at 5-10°C[3,8].

26. During filtration and washing it is not necessary to remove all of the precipitate from the flask. However, the glass beads should be transferred to the filter paper because they may cause some precipitation of hydrated molybdenum trioxide during the subsequent precipitation of phosphorus as ammonium phosphomolybdate.

27. Small amounts of phosphorus can be determined spectrophotometrically at this stage by the Phosphovanadomolybdic Acid-Isoamyl Alcohol Extraction Method (p 81), after the addition of iron (III) solution and perchloric acid to the solution, or to a suitable aliquot of the solution, followed by evaporation of the solution to fumes of perchloric acid to remove excess nitric acid.

28. Because ammonium nitrate is formed during the neutralization of nitric acid with ammonium hydroxide, the addition of 10 g,as recommended in Procedure A(a), is not necessary in this procedure.

29. To avoid loss of sample resulting from the rapid reaction between carbonates and acid, moisten the sample with approximately 10 ml of water, cover the beaker, and slowly

add concentrated nitric acid in small portions. When the decomposition of the carbonates is complete, add the recommended amounts of hydrochloric and perchloric acids, and proceed as described.

30. If any residue (i.e., titanium and zirconium phosphates) is still present at this stage, it should be quantitatively removed by filtration, ignited, and fused with sodium carbonate. After digestion of the melt in water, filter the resulting solution and add the filtrate to the initial filtrate. Boil the combined solution to expel carbon dioxide, then proceed as described.

31. The addition of iron (III) solution to co-precipitate phosphorus is not necessary if the sample contains an equivalent amount (i.e., 120 mg) or more of iron and/or aluminum.

Calculations

Normality of sodium hydroxide solution (N_{NaOH})

$$= \frac{\text{Weight of potassium acid phthalate (g)}}{0.2042 \times V}$$

where:

V = volume (ml) of sodium hydroxide solution required by the potassium acid phthalate.

Phosphorus equivalent (mg/ml) of the sodium hydroxide solution (P_{EQ})

$$= N_{NaOH} \times \frac{1}{23} \times 30.97$$

Normality of nitric acid solution (N_{HNO_3}) $= \dfrac{V \times N_{NaOH}}{v}$

where:

V = Volume (ml) of sodium hydroxide solution required by "v" ml of nitric acid solution.

Sodium hydroxide equivalent (ml/ml) of the nitric acid solution ($NaOH_{EQ}$)

$$= \frac{N_{HNO3}}{N_{NaOH}} \quad \text{OR} \quad \frac{V}{v}$$

where:

V and v are as described above.

%P

$$= \frac{[(V_S - NaOH_{EQ} x v_S) - (V_B - NaOH_{EQ} x v_B)] \; xP_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of sodium hydroxide solution added to the sample.

v_S = volume (ml) pf nitric acid solution required by the excess sodium hydroxide solution added to the sample.

V_B = volume (ml) of sodium hydroxide solution added to the blank.

v_B = volume (ml) of nitric acid solution required by the excess sodium hydroxide solution added to the blank.

% P_2O_5 = 2.291 x %P

Other applications

The method described in Procedure A(b) can probably be employed to determine phosphorus in chromium ores and mill products.

References

1. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E278-71, pp 762-765 (1971).

2. Technical Committee 102 - Iron Ores, "Determination of Phosphorus Content", International Organization for Standardization, Document 105E, March (1970).

3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 694-710 (1953).

4. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Company, New York, pp 390-397 (1948).

5. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 5, 334 (1961).

6. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 83-85 (1938).

7. Idem, ibid., pp 70-71 (1938).

8. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E 31-67, pp 96-97 (1971).

DETERMINATION OF TOTAL SULPHUR IN ORES AND MILL PRODUCTS BY THE DIRECT-COMBUSTION METHOD

Principle

This method[1-3] is based on the oxidation of elemental and sulphide sulphur, and the decomposition of inorganic sulphates and sulphites to sulphur dioxide and some sulphur trioxide by combustion of the sample in a water- and sulphur oxide-free oxygen atmosphere. The resultant gases are absorbed in a neutral silver nitrate solution. Sulphur is determined by titration of the resultant nitric and sulphuric acids, formed during the reaction of sulphur dioxide and sulphur trioxide with silver nitrate and water, respectively, with sodium hydroxide[4], in the presence of methyl red and Xylene Cyanole FF as internal indicators.

The corresponding reactions for the absorption and titration processes are:

$$SO_2 + 2AgNO_3 + H_2O \rightarrow Ag_2SO_3\downarrow + 2HNO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O.$$

Outline

The sample is ignited at approximately 1450°C in a water- and sulphur oxide-free oxygen atmosphere. The resulting sulphur dioxide and trioxide are collected in a neutral silver nitrate solution. The nitric and sulphuric acids in the resulting solution are titrated with sodium hydroxide solution.

Discussion of interferences

Chlorine and fluorine, which are produced during the combustion of samples containing fluoride and chloride compounds, interfere in this method because they readily oxidize sulphur dioxide to sulphur trioxide in the presence of water. This reaction results in the formation of sulphuric, hydrochloric, and hydrofluoric acids, and causes high results for sulphur because the hydrofluoric acid, and the nitric acid that is produced by the reaction of hydrochloric acid with the silver nitrate solution employed for the absorption of the sulphur oxides, are also titrated with the sodium hydroxide solution[5]. Nitrates, molybdenum, arsenic, selenium, and tellurium interfere because they are volatilized as oxides during the combustion of sulphur, and subsequently form soluble acidic compounds that react with the titrant[6,7].

Water causes low results for sulphur because it reacts with sulphur oxides to form acids that condense in the exit tube[7]. Interference from hygroscopic moisture (H_2O^-) can be eliminated by drying the sample at 105-110°C prior to the determination of sulphur. The method is not applicable to samples containing combined water (H_2O^+).

Iron oxide dust and part of the volatile acidic oxides (e.g., molybdenum trioxide) are removed by passing the sulphur oxides through a glass tube filled with dry cotton-wool. Up to approximately 1% by weight of molybdenum does not cause significant error in the sulphur result[2].

A purification unit containing Ascarite (asbestos impregnated with sodium hydroxide) and anhydrous magnesium perchlorate removes sulphur oxides and water, respectively, from the oxygen employed for combustion and as the carrier gas.

Range

The method is suitable for samples containing approximately 0.01 to 5% of sulphur, but material containing higher concentrations can be analyzed with reasonable accuracy if more concentrated (e.g., 0.1-0.2 N) sodium hydroxide solution is employed as titrant.

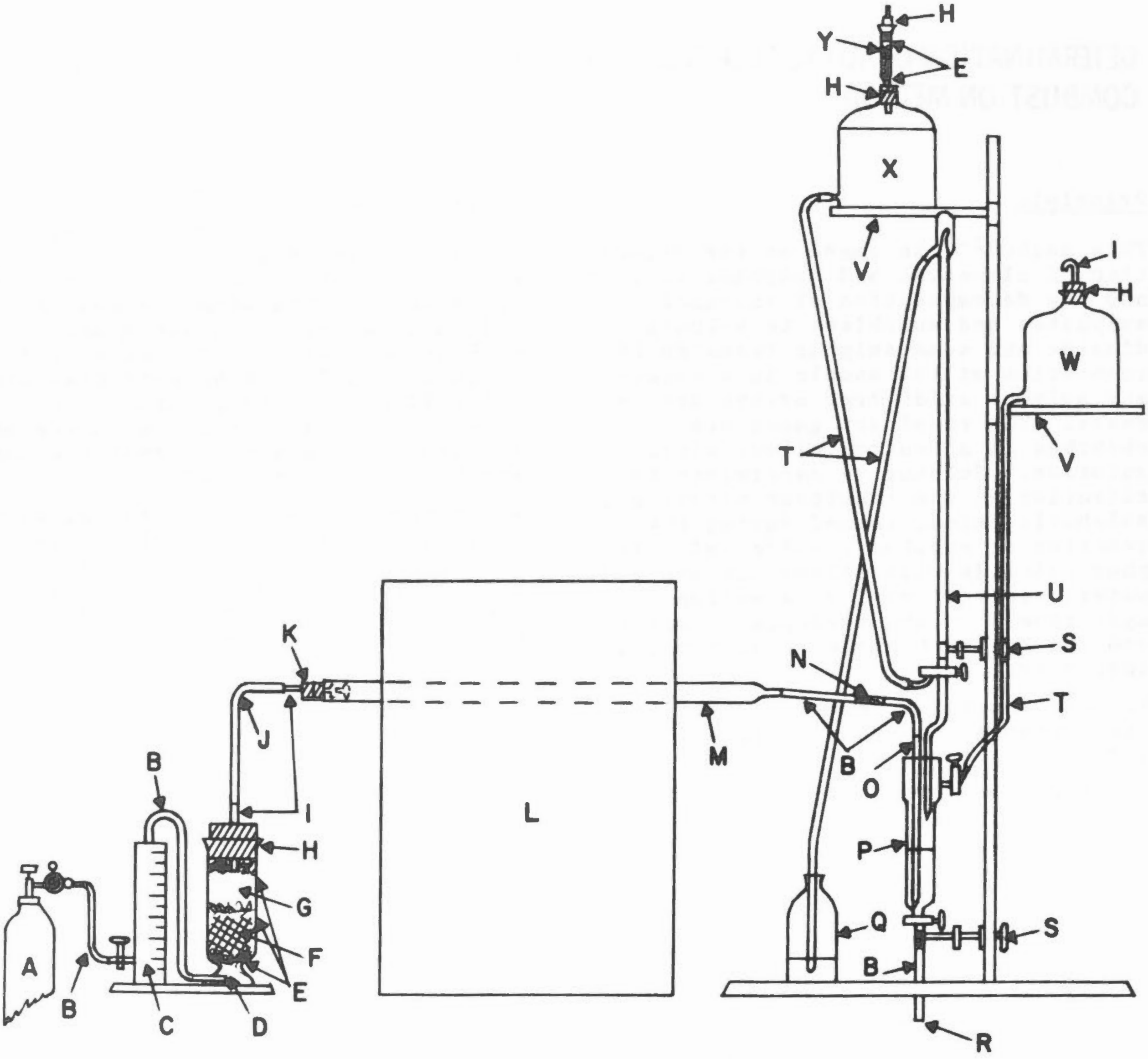

FIGURE 1. Apparatus for the determination of total sulphur by direct-combustion

A - Oxygen tank with two-stage regulator.
B - Rubber tubing.
C - Oxygen-flow meter.
D - Purification unit containing Ascarite (20-30 mesh) and anhydrous magnesium perchlorate (Anhydrone).
E - Glass-wool.
F - Ascarite.
G - Anhydrous magnesium perchlorate.
H - Rubber stopper.
I - Glass tube.
J - Tygon tubing (approximately 2.5 ft).
K - Rubber stopper with oxygen (heat-deflector) baffle.
L - Electric furnace, resistance-type with appropriate temperature controls, or induction-type with appropriate power input indicating device.
M - Combustion tube, high-temperature.
N - Glass fume- and dust-trap tube filled with dry cotton-wool.
O - Glass gas-bubbler tube.
P - Titration vessel (approximately 200 ml capacity) marked at 65 ml.
Q - Sodium hydroxide overflow bottle.
R - Drain for titration vessel.
S - Clamp.
T - Tygon tubing.
U - Burette (automatic Shellbach-type, 50 ml capacity).
V - Bottle platform.
W - Bottle (brown) containing silver nitrate solution.
X - Bottle containing sodium hydroxide solution.
Y - Carbon dioxide-guard tube containing Ascarite (20-30 mesh).

Apparatus

Apparatus for the determination of total sulphur by direct combustion. A typical arrangement of the apparatus is illustrated in Figure 1. Various types of specialized apparatus that are commercially available have been reviewed in the literature[8], but a suitable apparatus can also be readily constructed in the laboratory. The following general recommendations indicate the types of apparatus and related materials that are acceptable[9]:

(a) *Combustion apparatus* - Any electric tube-furnace capable of continuous operation at 1425-1450°C may be employed, and the combustion can be accomplished either by resistance or induction heating. If an induction-type furnace is employed, a rheostat to control the power input to the induction coil is required to avoid heating some types of samples too rapidly during the early stages of combustion. The combustion zone of the resistance-type furnace must be 20-25 cm (8-10 in.) in length, and that of the induction-type furnace must provide amply for adequate heating of the sample.

(b) *Combustion tubes* - The combustion tube must be a low-sulphur refractory type (e.g., synthetic zircon) that can withstand the maximum operating temperature without becoming porous, and should preferably be tapered at one end. Tubes approximately 30 inches long, with an inside diameter of 1.25 inches, are generally used with resistance furnaces.

(c) *Combustion boats and covers* - The boats, crucibles and covers (Note 1) employed with the respective types of furnaces should be essentially sulphur-free. Prior to use they should be pre-ignited in oxygen in the combustion tube, at 1425-1450°C, for at least 2 minutes, then cooled and stored in a dessicator to prevent the adsorption of sulphur gases or fumes from the air.

(d) *Oxygen-purification unit* - The purity of the oxygen should be not less than 99.5%. It should be passed through two reduction pressure valves (approximately 30 and 2 to 4 psi, respectively) or a suitable two-stage reduction valve to provide a steady and adequate flow. Water and sulphur oxides should be removed by passing the gas through anhydrous magnesium perchlorate and Ascarite, respectively.

(e) *Connections* - A metal breech connector at the entrance of the combustion tube is recommended. If a rubber stopper (illustrated in Figure 1) is used, it must be protected by heat-reflecting baffles, preferably of the double-disk type. Connection between the outlet end of the combustion tube and the absorption and titration assembly should be as short and free of bends as possible. All rubber stoppers and tubing employed for connections must be essentially sulphur-free.

(f) *Absorption and titration assembly.* The apparatus (e.g., the Dietert titration unit - illustrated in Figure 1) should consist of an absorption and titration vessel of appropriate volume and shaped to effect complete absorption of sulphur oxides in a small volume of solution.

Reagents

Sodium hydroxide stock solution, 0.05 N. Transfer 2.000 g of sodium hydroxide to a 300-ml Erlenmeyer flask, and add approximately 100 ml of water and 0.1 g of barium hydroxide to precipitate any carbonate present. Stopper, and shake until the sodium hydroxide has dissolved, then allow the solution to stand for at least 24 hours. Filter the resulting solution (Whatman No. 42 paper) and wash the paper thoroughly with carbon dioxide-free water. Dilute the filtrate to 1 litre with carbon dioxide-free water, and store in a polyethylene bottle.

Standard sodium hydroxide solution, 0.005 N. Dilute 100 ml of the stock solution to 1 litre with carbon dioxide-free water, and protect the solution from atmospheric carbon dioxide by means of a guard tube containing Ascarite as shown in Figure 1.

Methyl red indicator solution, 0.1% w/v in ethyl alcohol.

Xylene cyanole FF indicator solution, 0.1% w/v.

Silver nitrate solution, 0.34% w/v. Dissolve 3.4 g of the reagent in approximately 400 ml of water, add 7 ml each of 0.1% methyl red and 0.1% xylene cyanole FF indicator solutions and dilute to 1 litre with water.

Water (carbon dioxide-free). Freshly boiled and cooled water.

Standardization of sodium hydroxide solution

Standardize the dilute 0.005 N sodium hydroxide solution by carrying 0.05-1 g of a sample of ore of known sulphur content, similar in type and containing approximately the same amount of sulphur as that present in the sample taken for analysis (Note 2), through the described procedure. Calculate the sulphur equivalent (mg/ml) of the sodium hydroxide solution (Note 3).

Procedure

Heat the furnace to 1425-1450°C and, by means of the upper stopcock in the titration vessel P (Figure 1), add 65 ml of 0.34% silver nitrate solution to the vessel (Notes 4 and 5). Place the gas-bubbler tube O in the titration vessel (Note 6), close the inlet end of the combustion tube (Note 7) with the rubber stopper K, and pass oxygen through the tube at a rate of approximately 1.5 litres per minute for 10-15 minutes to remove air and moisture from the apparatus. Maintain the flow of oxygen and, from the burette U, add sufficient standard sodium hydroxide solution to the titration vessel, by drops, until the purple colour has disappeared and the solution is clear green. Record the volume of titrant required to reach this first end-point.

Open the inlet end of the combustion tube, and quickly insert a previously-ignited covered boat or crucible (Note 8) containing 0.05-1 g of dry powdered sample (Notes 9 and 10), containing up to approximately 4 mg of sulphur, into the tube. Push the boat or crucible into the hot central zone with a steel rod and immediately close the tube. Continue to pass oxygen through the tube at a rate of approximately 1.5 litres per minute for 5 minutes, maintain the flow of oxygen, and again titrate the solution in the titration vessel to a clear green end-point (Note 11). Correct the total volume of titrant required for the titration by subtracting that required to reach the first end-point (Note 12).

Notes

1. The cover employed with boats used in the resistance-type furnace is usually a sleeve-type, open at both ends to allow free access of oxygen. That employed with crucibles used in some induction furnaces is a round porous-type. The cover prevents damage to the combustion tube if the sample spatters during the combustion process.

2. Because the proportion of sulphur evolved as the oxides varies with different sample materials and with the amount of sulphur present, and because the evolution of the oxides is not quite quantitative, the sodium hydroxide solution must be standardized empirically, preferably using the same weight of a similar type of sample of known sulphur content, and containing approximately the same amount of sulphur as that present in the sample[1,3]. If a standard ore sample containing approximately the same amount of sulphur is not available, a suitable standard sample can be prepared by mixing appropriate amounts of standard samples of higher and lower sulphur contents.

For the routine determination of large amounts of sulphur, in which high accuracy is not required, the sodium hydroxide solution can be standardized against any ore sample (but preferably of the same type) of known (i.e., high or low) sulphur content. The weight of the standard sample taken need not be the same as that of the sample taken for analysis, but the amount of sulphur present in both samples should be approximately the same.

3. Theoretically 1 ml of 0.005 N sodium hydroxide solution = 0.0802 mg of sulphur, but because the evolution of sulphur oxides is not quite quantitative (Note 2) the sulphur equivalent found will be slightly less than the above value. Regardless of whether nitric acid, formed by the reaction of sulphur dioxide with silver nitrate, or sulphuric acid, formed by the reaction of sulphur trioxide with water, are being titrated, there is no change

in the sulphur equivalent because the number of moles of nitric and sulphuric acids that are formed per mole of sulphur during the above reactions (i.e., 2 moles and 1 mole, respectively) both combine with 2 moles of sodium hydroxide[4].

4. The volume of silver nitrate solution taken, the time and temperature of combustion, and the oxygen flow rate employed for the analysis of the sample must be the same as those employed for the standardization of the sodium hydroxide solution, or else the result obtained for the sample will not be accurate[3].

5. Instead of absorbing the evolved sulphur oxides in dilute silver nitrate solution, sulphur dioxide (but not sulphur trioxide) can be absorbed in a dilute hydrochloric acid-starch-potassium iodide solution, followed by oxidation of the dioxide to sulphuric acid with iodine, produced by titration of the solution with standard potassium iodate solution[2,3,6]. Alternatively, sulphur dioxide can be absorbed in the above solution in the presence of an excess of standard potassium iodate solution, followed by titration of the excess liberated iodine with standard sodium thiosulphate solution[1,10,11]. Sulphur dioxide and sulphur trioxide can also be absorbed in dilute hydrogen peroxide, followed by titration of the resultant sulphuric acid with standard sodium hydroxide or sodium borate solution[2,6]. Chlorine and fluorine interfere in all of the above titration procedures.

6. If the inner walls of the titration vessel become coated with white silver sulphite after numerous analyses, the vessel can be cleaned with aqua regia.

7. If the sulphur equipment is in frequent use, the residue that accumulates in the cooler part of the combustion tube should be burned out either daily or weekly after disconnecting the exit tube. This can be accomplished by moving the cooler part of the tube into the hot central zone of the furnace and allowing oxygen to flow through the tube for 15-20 minutes. If the residue is allowed to accumulate, the yield of sulphur oxides is reduced during combustion because the residue absorbs sulphur oxides[1,12].

8. To avoid possible contamination and moisture (Note 9) from the hands, the pre-ignited boat or crucible and cover should be handled with clean tongs or forceps.

9. The sample must be free of moisture or else low results will be obtained because of the retention of sulphur oxides by water vapour which condenses in the glass fume- and dust-trap N and in the connecting rubber exit tubes. If the sample is suspected to contain moisture, it should be dried at 105-110°C for approximately 1 hour, prior to the determination of sulphur. Previously weighed dried samples that have been transferred to the combustion boat or crucible should be covered and stored in a dessicator until required. This also prevents contamination of the sample from atmospheric dust.

10. If necessary (e.g., with an induction furnace), low-sulphur iron chips or powder, and tin granules (30-mesh) can be employed as accelerators to promote combustion and to form a conductible mass[3]. If these fluxes are employed, a blank determination should be carried out, using the same amount of iron and tin as that employed for the sample, and the result obtained should be subtracted from that obtained for the sample.

11. If a definite end-point cannot be obtained, the cotton-wool in the glass fume- and dust-trap N should be changed, and the tube should be cleaned and dried. Only dried cotton-wool, handled with clean tongs or forceps, should be employed.

12. Standardization of the sodium hydroxide solution with appropriate standard samples, if necessary, and the determination of sulphur in other samples can be carried out in succession at this stage, as described in the procedure, if the flow of oxygen is maintained throughout the course of the analyses. Fresh silver nitrate solution should be employed for each determination.

Calculations

Sulphur equivalent (mg/ml) of the 0.005 N sodium hydroxide solution (S_{EQ})

$$= \frac{\text{Weight of sulphur in the standard sample taken (mg)}}{V - v}$$

where:

V = total volume (ml) of sodium hydroxide solution required for the titration.

v = volume (ml) of sodium hydroxide solution required to reach the first end-point.

$$\% \ S = \frac{(V - v) \times S_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V and v are as described above.

Other applications

This method can be employed to determine sulphur in iron, steel, and ferrous and non-ferrous alloys[2,4,6,13], and in silicate and carbonate rocks and minerals, if suitable standard materials are available and if iron and tin are used as accelerators to promote combustion[10-12].

References

1. W.G. Rice-Jones, Anal. Chem., 25, 1383 (1953).
2. H. Green, Br. Cast Iron Res. Assoc. J., 11, 76 (1963).
3. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E 395-70, pp 965-967 (1971).
4. K. Swoboda, Z. Anal. Chem., 77, 269 (1929).
5. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 7, 20 (1961).
6. E.C. Pigott, "Ferrous Analysis - Modern Practice and Theory", 2nd ed., Chapman and Hall, Ltd., London, pp 453-456, 459-461, 465 (1953).
7. J.F. Chapman and M. Thackray, Anal. Chem., 40, 202 (1968).
8. B. Nebesar, J. Chem. Educ., 49, A63 (1972).
9. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, E50-68, pp 302-305 (1971).
10. J.G. Sen Gupta,Anal. Chim. Acta, 49, 519 (1970.
11. J.A. Maxwell, "Rock and Mineral Analysis", Interscience, New York, pp 443-445 (1968).
12. M.E. Coller and R.K. Leininger, Anal. Chem., 27, 949 (1955).
13. American Society for Testing and Materials, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores", Part 32, pp 454-455, 839-842 (1971).

DETERMINATION OF TIN IN ORES AND MILL PRODUCTS BY THE IODIMETRIC METHOD AFTER REDUCTION WITH METALLIC IRON

Principle

This method[1] is based on the reduction of tin to the divalent state with metallic iron in an approximately 4.7 M hydrochloric acid medium and an air-free atmosphere. Tin is determined by titration of the resultant tin (II) with iodine (formed by the reaction of potassium iodate and potassium iodide in an acid medium), in a carbon dioxide atmosphere, in the presence of Thyodene (soluble starch) as internal indicator.

The corresponding reactions for these processes are:

$$SnCl_4 + Fe \rightarrow SnCl_2 + FeCl_2$$

$$KIO_3 + 5KI + 6HCl \rightarrow 3I_2 + 3H_2O + 6KCl$$

$$SnCl_2 + I_2 + 2HCl \rightarrow SnCl_4 + 2HI.$$

Outline

The sample is decomposed by fusion with sodium carbonate and sodium peroxide. The melt is dissolved in dilute hydrochloric acid, and tin, iron, and certain other elements are ultimately precipitated as the hydrous oxides with ammonium hydroxide, and separated from copper, molybdenum, and some tungsten by filtration. After dissolution of the precipitate, tin is re-precipitated to remove occluded copper and molybdenum, and the precipitate is dissolved in dilute hydrochloric-hydrofluoric acid solution. The tin in the resulting solution is ultimately reduced with iron metal, and titrated with potassium iodate solution containing potassium iodide.

Discussion of interferences

Molybdenum interferes in the titration of tin because it is reduced to a lower oxidation state by metallic iron, and is subsequently oxidized by the iodine. Copper, arsenic, antimony, and bismuth interfere because they are reduced to the elemental state and obscure the end-point of the titration[1-3].

Interference from copper and molybdenum is eliminated by separating tin from these elements by precipitation as the hydrous oxide with ammonium hydroxide. Tungsten is not completely separated from tin by this procedure, but the blue compound formed by reduction with iron does not react with iodine, and interferes only if it masks the blue colour of the starch-iodine end-point[2,3].

Small amounts of arsenic, antimony, and bismuth, and moderate amounts of other elements (e.g., titanium, zirconium, and aluminum) that precipitate as hydrous oxides, or are co-precipitated during the ammonium hydroxide separation of tin, do not interfere in the reduction and subsequent titration of tin[2,3]. Interference from large amounts of elemental arsenic, antimony, and bismuth, which are formed during the reduction procedure, can be avoided by repeating the reduction step, after the removal of the precipitated elements by filtration[1].

Range

The method is suitable for samples containing more than approximately 1% of tin.

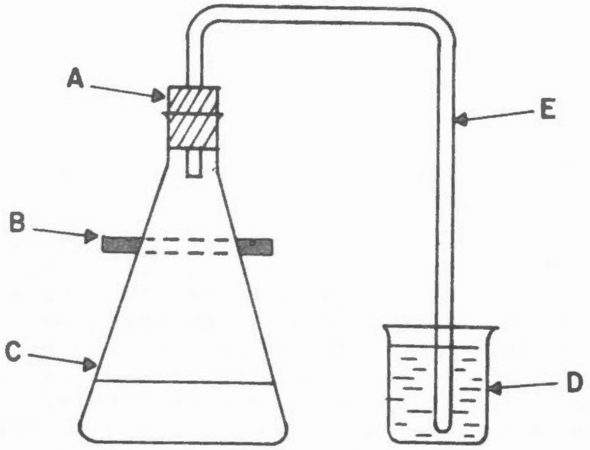

FIGURE 1. Apparatus for the reduction of tin

A - Rubber stopper.
B - Lead weight.
C - Reduction flask (500-ml Erlenmeyer-type).
D - Beaker (250-ml) containing saturated sodium bicarbonate solution.
E - Glass siphon tube.

Apparatus

Apparatus for the reduction of tin. Illustrated in Figure 1.

Reagents

Standard potassium iodate solution, 0.05 N. Dissolve 3.5670 g of potassium iodate, 10 g of potassium iodide, and 2 g of sodium hydroxide in water and dilute to 2 litres.

Standard tin solution (1 ml = 3 mg of tin). Dissolve 1.5000 g of high-purity tin metal by heating gently in a covered 400-ml beaker with 50 ml of concentrated hydrochloric acid. Cool the resulting solution, add an additional 50-ml portion of concentrated hydrochloric acid, transfer the solution to a 500-ml volumetric flask, and dilute to volume with water.

Iron granules, high-purity.

Thyodene (soluble starch) indicator solution, 5% w/v. Dissolve 5g each of Thyodene and potassium iodide in water, and dilute to 100 ml. Prepare fresh as required.

Antimony trichloride solution, 1% w/v in concentrated hydrochloric acid.

Hydrochloric-hydrofluoric acid solution, 50% and 2% v/v, respectively. Store in a polyethylene bottle.

Hydrochloric acid, 50% v/v.

Sodium bicarbonate solution, saturated.

Sodium bicarbonate tablets (10 grains).

Standardization of potassium iodate solution

Transfer a 20-40-ml aliquot of the standard tin solution to a 500-ml Erlenmeyer reduction flask (Figure 1), add sufficient concentrated hydrochloric acid so that approximately 80 ml are present, and dilute the solution to approximately 200 ml with water. Add 5 g of iron granules and 5-10 drops of 1% antimony trichloride solution (Note 1), and boil the solution gently on a hot-plate until most, but not all of the iron granules are dissolved. Cap the flask with the rubber stopper A fitted with the siphon tube, immerse the outlet end of the tube in a beaker containing saturated sodium bicarbonate solution, and continue boiling the solution until several minutes after the dissolution of the remaining iron granules (Note 2). Remove the flask from the hot-plate - with the outlet tube still immersed in the sodium bicarbonate solution - and place the lead weight B around the neck of the flask. Cool the resulting solution in a water-bath maintained at room temperature, and finally in an ice-bath (Note 3). Remove the cap of the flask, add two sodium bicarbonate tablets (Note 4) and 10 ml of 5% Thyodene solution, and immediately titrate the solution with standard potassium iodate solution to the blue starch-iodine end-point (Note 5). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure (Note 6). Determine the normality of the potassium iodate solution, and calculate the tin equivalent (mg/ml) (1 ml of 0.05 N potassium iodate solution = 2.967 mg of tin).

Procedure

Transfer 0.2-2 g of powdered sample, containing up to approximately 150 mg of tin, and 3-4 g each of sodium carbonate and sodium peroxide to a

50-ml zirconium crucible. Mix thoroughly and cover the mixture with a thin layer of sodium peroxide. Cover the crucible with a zirconium cover, fuse the contents over a blast burner, and keep the melt at red heat for several minutes to ensure complete sample decomposition. Allow the melt to cool for approximately 5 minutes, then transfer the crucible and cover to a 600-ml (covered) beaker containing 100 ml of water. When the subsequent reaction has ceased, remove the crucible and cover after washing them thoroughly with concentrated hydrochloric acid and water, and neutralize the solution approximately with concentrated hydrochloric acid. Add 5 ml in excess and dilute the solution to approximately 400 ml with water.

Boil the resulting solution for about 5 minutes to remove the carbon dioxide and hydrogen peroxide formed during the acidification step, then, using litmus paper, neutralize the solution approximately with concentrated ammonium hydroxide to precipitate the hydrous oxides of tin and iron. Add 5 ml of ammonium hydroxide in excess and boil the solution for several minutes to coagulate the precipitate. Allow the precipitate to settle, then filter the solution (Whatman No. 541 paper) and wash the beaker, paper, and precipitate thoroughly with hot water. Discard the filtrate and washings.

Using a jet of hot water, transfer the bulk of the precipitate to the beaker in which the precipitation was carried out. Dissolve the small amount of precipitate remaining on the filter paper, using hot 50% hydrochloric acid, and wash the paper thoroughly with hot water to remove the excess acid (Notes 7 and 8). Collect the resulting solution in the beaker containing the precipitate. If necessary, add sufficient concentrated hydrochloric acid to dissolve the precipitate, then add 5 ml in excess, and re-precipitate the hydrous oxides as described above. Filter the hot solution through the original filter paper, wash the beaker, paper, and precipitate thoroughly with hot water, and again transfer the bulk of the precipitate to the beaker in which the precipitation was carried out. Dissolve the precipitate remaining on the paper by repeated washing of the paper with hot 50% hydrochloric-2% hydrofluoric acid solution followed by hot water, and collect the solution in the beaker containing the precipitate.

Add sufficient concentrated hydrochloric acid to the resulting solution so that approximately 80 ml are present (Note 9), and transfer it to a reduction flask. Dilute the solution to approximately 200 ml with water, and proceed with the reduction (Notes 10 and 11) and subsequent titration of tin as described above. Correct the result obtained for the sample by subtracting that obtained for a blank that is carried through the reduction procedure (Note 12).

Notes

1. Antimony trichloride catalyzes the reduction of tin (IV) with metallic iron[1].

2. Although tin (II) is readily air-oxidized to the tetravalent state, capping of the reduction flask at the beginning of the reduction step is not necessary because the steam evolving during the boiling process prevents air from entering the flask. Furthermore, if the flask is capped at this stage, and the outlet tube is placed in a solution of sodium bicarbonate, the hydrochloric acid that distils over during the boiling process will neutralize the bicarbonate solution.

3. If the solution is cooled too rapidly, sodium bicarbonate solution will occasionally siphon back into the reduction flask. This can be avoided by using a slow stream of carbon dioxide or nitrogen gas to maintain an air-free atmosphere in the flask during both the reduction and cooling stages.

4. The carbon dioxide formed by the dissolution of the sodium bicarbonate tablets in the acid solution helps to exclude air from the flask during the titration of tin (II).

5. A 40-ml portion of the tin solution (i.e., 120 mg of tin) requires 40.44 ml of 0.05 N potassium iodate solution.

6. The magnitude of the blank depends on the amount and purity of the iron used for the reduction of tin.

7. Complete removal of the excess acid can be ensured by washing the paper with dilute ammonium hydroxide. The excess acid must be removed from the paper to avoid loss of tin during the subsequent filtration step. The original filter paper should be used for the second filtration step because small amounts of the hydrous oxide of tin (IV) are strongly held in the fibres of filter paper[3]; this residual tin is not readily dissolved when the mixed hydrous oxide precipitate remaining on the paper is treated with 50% hydrochloric acid. The residual tin is removed from the paper, after the second precipitation of the hydrous oxides, by washing the paper with 50% hydrochloric acid containing hydrofluoric acid. This wash solution cannot be used to dissolve the initial precipitate because fluoride ion complexes tin (IV) and, consequently, would prevent its re-precipitation as the hydrous oxide.

8. If the sample contains only small amounts of copper, molybdenum, and/or tungsten, the subsequent re-precipitation of the hydrous oxides may not be necessary. In this case, dissolve the precipitate remaining on the filter paper with 50% hydrochloric-2% hydrofluoric acid solution, and proceed as described with the reduction and subsequent titration of tin.

9. Any gelatinous silica that is present in the solution can be dissolved by the addition of several drops of concentrated hydrofluoric acid.

10. The presence of tungsten or molybdenum is indicated during the reduction step by the blue or brown colour of the solution, respectively.

11. If the sample contains an appreciable amount of arsenic, antimony, and/or bismuth (e.g., a sulphide concentrate), as indicated by the precipitation of the respective elements or metals during the reduction step, boil the solution gently until all of the iron granules have dissolved. Filter the solution (Whatman No. 541 paper) into a second reduction flask, and wash the flask, paper, and precipitate with hot water. Discard the paper and precipitate, and repeat the reduction procedure (Note 12).

12. If the reduction procedure has been repeated, the result obtained for the sample must be corrected by subtracting that obtained for a blank that is treated in a similar manner (Note 6).

Calculations

Normality of potassium iodate solution (N_{KIO_3})

$$= \frac{\text{Weight of tin in aliquot taken (g)}}{0.05935 \times (V - v)}$$

where:

V = volume (ml) of potassium iodate solution required by the tin.

v = volume (ml) of potassium iodate solution required by the blank.

Tin equivalent (mg/ml) of the potassium iodate solution (Sn_{EQ})

$$= N_{KIO_3} \times \frac{1}{2} \times 118.7$$

OR

$$= \frac{\text{Weight of tin in aliquot taken (mg)}}{V - v}$$

where:

V and v are as described above.

$$\% \text{ Sn} = \frac{(V_S - V_B) \times Sn_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of potassium iodate solution required by the sample.

V_B = volume (ml) of potassium iodate solution required by the blank.

$\% \text{ SnO}_2 = 1.270 \times \% \text{ Sn}$

References

1. R.C. McAdam and D.J. Charette, "The Determination of Tin in Ores and Mill Products (Volumetric-Potassium Iodate Method)", Dept. of Energy, Mines and Resources, Mines Branch, Mineral Sciences Division, Ottawa, Internal Report MS 66-59, August (1966).

2. W.A. Dupraw, Anal. Chem., 26, 1642 (1954).

3. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, pp 287-292 (1953).

DETERMINATION OF TITANIUM IN TITANIUM ORES AND MILL PRODUCTS BY TITRATION WITH FERRIC AMMONIUM SULPHATE AFTER REDUCTION WITH METALLIC ALUMINUM

Principle

This method[1,2] is based on the reduction of titanium to the trivalent state with metallic aluminum in a sulphuric-hydrochloric acid medium and an air-free atmosphere. Titanium is determined by titration of the resultant titanium (III) with ferric ammonium sulphate, in a carbon dioxide atmosphere, in the presence of potassium thiocyanate as internal indicator.

The corresponding reactions for these processes are:

$$6Ti(SO_4)_2 + 2Al \rightarrow 3Ti_2(SO_4)_3 + Al_2(SO_4)_3$$

$$Ti_2(SO_4)_3 + 2FeNH_4(SO_4)_2 \rightarrow 2Ti(SO_4)_2 + 2FeSO_4 + (NH_4)_2SO_4.$$

Outline

The sample is decomposed by fusion with potassium pyrosulphate or sodium peroxide, depending on the absence or presence of titanium silicates, respectively. After dissolution of the melt, the titanium in the resulting solution is reduced with aluminum metal and titrated with ferric ammonium sulphate solution.

Discussion of interferences

Vanadium, tin, chromium, molybdenum, platinum, tungsten, and niobium interfere in this method because they are reduced to lower valence states by metallic aluminum, and subsequently oxidized by ferric ammonium sulphate[1,2]. Copper, arsenic, and antimony are reduced to the elemental state and interfere during titration by obscuring the orange or faint red iron (III)-thiocyanate complex endpoint[1].

Range

The method is suitable for samples containing more than approximately 0.5% of titanium.

Apparatus

Apparatus for the reduction of titanium. Illustrated in Figure 1 (p 356) of the Volumetric-Iodimetric Method for tin.

Reagents

Standard ferric ammonium sulphate solution, 0.06 N. Transfer 28.9326 g of ferric ammonium sulphate dodecahydrate [$FeNH_4(SO_4)_2 \cdot 12H_2O$] to a 600-ml beaker, add approximately 300 ml of water and 50 ml of 50% sulphuric acid and stir to dissolve. Transfer the resulting solution to a 1-litre volumetric flask, and dilute to volume with water.

Potassium thiocyanate indicator solution, 45% w/v.

Aluminum foil, high-purity.

Sulphuric acid, 50% v/v.

Sodium bicarbonate solution, saturated.

Standardization of ferric ammonium sulphate solution

Transfer 0.2000 g of pure titanium dioxide to a 500-ml Erlenmeyer reduction flask, add 8 g of ammonium sulphate and 20 ml of concentrated sulphuric acid, and heat the mixture over an open flame until decomposition is complete. Allow the flask and contents to cool to room temperature, then carefully add 130 ml of water in small portions. Add 20 ml of concentrated hydrochloric acid, and boil the solution for several minutes. Remove the flask from the vicinity of the burner and swirl it gently to release superheated steam. Add 1 g of aluminum foil, immediately cap the flask with the rubber stopper fitted with the siphon tube, and immerse the outlet end of the tube in a 250-ml beaker containing saturated sodium bicarbonate solution (Note 1). When all of the aluminum has dissolved, boil the solution gently for 3-5 minutes - with the outlet tube still immersed in the sodium bicarbonate solution - then place the lead weight around the neck of the flask, and cool the solution to less than 60°C (Note 2) in a water-bath. Remove the cap of the flask, add 2 ml of 45% potassium thiocyanate solution, and immediately titrate the resulting solution with standard ferric ammonium sulphate solution to a light orange or faint red end-point (Note 3). Correct the result obtained by subtracting that obtained for a blank that is carried through the reduction procedure (Note 4). Determine the normality of the ferric ammonium sulphate solution, and calculate the titanium equivalent (mg/ml) (1 ml of 0.06 N ferric ammonium sulphate solution = 2.874 mg of titanium).

Procedures

In these procedures a reagent blank is carried along with the samples.

Titanium silicates absent

Transfer 0.1-0.5 g of powdered sample, containing up to approximately 100 mg of titanium, to a dry 500-ml reduction flask containing 15 g of potassium pyrosulphate, and fuse the mixture over an open flame for approximately 30 minutes. Cool, add 130 ml of water, 30 ml of 50% sulphuric acid, and 25 ml of concentrated hydrochloric acid, and boil to dissolve the melt (Note 5). Remove the flask from the vicinity of the burner, swirl it gently to release superheated steam, then add 3 g of aluminum foil (Note 6) and proceed with the reduction and subsequent titration of titanium as described above. Correct the result obtained for the sample by subtracting that obtained for the reagent blank.

Titanium silicates present

Transfer 0.1-0.5 g of sample to a 30-ml iron crucible, add 2-3 g of sodium peroxide and mix thoroughly. Cover the crucible with an iron cover, cautiously (to avoid spattering) fuse the mixture over a low flame, and maintain it in the molten state for 3-5 minutes to ensure complete sample decomposition (Note 7). Allow the melt to cool, then transfer the crucible and cover to a 400-ml (covered) beaker containing approximately 150 ml of water. When the subsequent reaction has ceased, add sufficient 50% sulphuric acid to dissolve the precipitate, then add approximately 5 ml in excess. Remove the crucible and cover after washing them thoroughly with water, and add 25 ml of concentrated hydrochloric acid to the resulting solution.

Transfer the solution to a reduction flask and add a small strip of aluminum foil. Place a short-stemmed funnel in the neck of the flask to prevent loss of sample by spraying, and heat the solution on a hot-plate to initiate the reaction. Remove the flask from the hot-plate, and continue adding small portions of aluminum foil until approximately 2 g have been dissolved (Note 8). Add 1 g of foil, immediately cap the flask with the rubber stopper fitted with the siphon tube and continue with the reduction and subsequent titration of titanium as described above.

Notes

1. Care should be taken that the beaker does not contain any solid sodium bicarbonate; this may block the siphon tube and could result in the explosion of the reduction flask. Because the dissolution of the aluminum foil is rapid, the reduction flask should be swirled, when the reaction is nearly complete, to ensure thorough mixing and complete reduction.

2. Decomposition of the potassium thiocyanate indicator occurs at temperatures exceeding 70°C[1]. During the cooling stage, the sodium bicarbonate solution is drawn into the Erlenmeyer flask and reacts with the acid to form carbon dioxide which prevents air-oxidation of the titanium (III).

3. A 0.2000-g portion of titanium dioxide (i.e., 119.9 mg of titanium) requires 41.72 ml of 0.06 N ferric ammonium sulphate solution.

4. A correction for a reagent blank is necessary to eliminate error resulting from the presence of small

amounts of titanium and tin in the aluminum metal. Aluminum metal containing copper, arsenic, and antimony should not be employed as reductant because these elements are reduced to the elemental state and subsequently interfere with the titration by obscuring the end-point[1].

5. Any insoluble residue that is present at this stage can be ignored unless it is suspected to contain titanium silicates. If titanium silicates are present, sample decomposition by fusion with sodium peroxide is recommended.

6. More aluminum is required for the reduction of titanium in an ore sample than for a comparable quantity of titanium dioxide. Ore samples contain an appreciable amount of iron, which is oxidized to the ferric state during fusion of the sample, and which must be reduced to the ferrous state before the reduction of titanium (IV) can proceed[1].

7. The crucible should be removed from the flame periodically and cooled by swirling. Over-heating results in rapid destruction of the crucible by the sodium peroxide.

8. Because excessive frothing occurs on the addition of aluminum foil, the reduction flask should not be capped until the frothing subsides and most of the ferric iron is reduced to the ferrous state. The foil should be added in small portions to maintain a continuous evolution of hydrogen gas.

Calculations

Normality of ferric ammonium sulphate solution $[N_{Fe(III)}]$

$$= \frac{\text{Weight of titanium dioxide (g)}}{0.07990 \times (V - v)}$$

where:

V = volume (ml) of ferric ammonium sulphate solution required by the titanium dioxide.

v = volume (ml) of ferric ammonium sulphate solution required by the blank.

Titanium equivalent (mg/ml) of the ferric ammonium sulphate solution $(Ti_{EQ}) = N_{Fe(III)} \times 47.90$

$$\% \text{ Ti} = \frac{(V_S - V_B) \times Ti_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of ferric ammonium sulphate solution required by the sample.

V_B = volume (ml) of ferric ammonium sulphate solution required by the blank.

$\% \text{ TiO}_2 = 1.668 \times \% \text{ Ti}$

Other applications

This method can be employed to determine titanium in titanium dioxide pigments, after sample decomposition with concentrated sulphuric acid and ammonium sulphate[1].

References

1. J.A. Rahm, Anal. Chem., 24, 1832 (1952).

2. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 5, pp 30-34, 49-51 (1961).

DETERMINATION OF VANADIUM IN MINERALS, ORES AND MILL PRODUCTS BY TITRATION WITH FERROUS AMMONIUM SULPHATE

Principle

This method[1-4] involves the oxidation of vanadium to the pentavalent state with potassium permanganate in an approximately 1 M sulphuric acid medium, the reduction of the excess permanganate with sodium nitrite, and the destruction of the excess nitrite with urea. Vanadium is determined by titration (reductimetric) of the resultant vanadium (V) with ferrous ammonium sulphate in the presence of sodium diphenylaminesulphonate as internal indicator, according to the reaction

$$VO_4^{-3} + Fe^{+2} + 6H^+ \rightarrow VO^{+2} + Fe^{+3} + 3H_2O.$$

Outline

Samples containing small amounts of silica are decomposed by fusion with sodium peroxide, and the melt is digested in water.

If cerium, selenium, tellurium, and large amounts of copper, nickel, cobalt, and chromium are absent, the solution is acidified with sulphuric acid, and tungsten, titanium, zirconium, niobium, and/or tantalum, if present, are complexed with hydrofluoric acid. Chromium (VI) is subsequently reduced with ferrous ammonium sulphate. The vanadium in the resulting solution is oxidized to the pentavalent state with potassium permanganate, and ultimately titrated with ferrous ammonium sulphate solution.

If cerium and large amounts of copper, nickel, and/or cobalt are present, the hydrous oxides of iron and the above elements are removed by filtration. After dissolution of the precipitate, the hydrous oxides are re-precipitated with sodium hydroxide to recover occluded vanadium. The filtrate is combined with the initial filtrate, and chromium is ultimately reduced to the trivalent state with hydrogen peroxide in an acetic acid medium. Vanadium is subsequently precipitated as lead vanadate and separated from sodium salts and chromium by filtration. After dissolution of the precipitate in dilute nitric acid, lead is converted to the sulphate, and nitric acid is removed by evaporation of the solution with sulphuric acid. If tungsten is absent, the vanadium in the resulting solution is ultimately oxidized with potassium permanganate and titrated as described above. If tungsten is present, hydrated tungsten trioxide is removed by filtration, dissolved in sodium hydroxide solution, and subsequently complexed with hydrofluoric acid. The resultant solution is added to the filtrate, and vanadium is determined as described above.

Samples containing large amounts of silica are decomposed with nitric, hydrochloric, hydrofluoric, and perchloric acids, and the solution is evaporated to fumes of perchloric acid. The acid-insoluble material is ultimately removed by filtration, ignited, and fused with sodium carbonate and potassium nitrate. The melt is dissolved in the initial filtrate and the solution is evaporated to fumes of perchloric acid to remove the resultant nitric acid.

If cerium and large amounts of copper, nickel, and cobalt are absent, chromium, if present in large amounts, is removed by volatilization as chromyl chloride. Depending on the absence or presence of tungsten, the vanadium in the resulting solution is ultimately determined as described above.

If cerium and large amounts of copper, nickel, and/or cobalt are present, iron and the above elements are precipitated as the hydrous oxides with sodium hydroxide, and separated from vanadium by filtration. After dissolution of the precipitate, the hydrous oxides are re-precipitated to recover occluded vanadium, and vanadium is subsequently separated from the excess sodium salts and chromium (III) by precipitation as lead vanadate, and determined as described above.

Discussion of interferences

Chromium (VI), cerium (IV), selenium (VI), and tellurium (VI) interfere in the determination of vanadium because they are also reduced to lower oxidation states by ferrous ammonium sulphate[1-4]. Large amounts of chromium (III), and other coloured ions [e.g., iron (III), copper (II), cobalt, and nickel] interfere by masking the green sodium diphenylaminesulphonate end-point[1,3,4]. Large amounts of sodium salts interfere in the oxidation and/or titration of vanadium and cause erroneous results[5].

Tungsten, if present as hydrated tungsten trioxide during the titration step, causes low results for vanadium because the precipitate partly adsorbs or occludes vanadium[1-4]. Tungsten also causes low results if it is present in a soluble reduced form during the ferrous ammonium sulphate reduction step, presumably because the reduced tungsten is not completely oxidized to the hexavalent state with potassium permanganate at room temperature, and subsequently reduces vanadium (V)[1]. During sample decomposition, tungsten is oxidized to the hexavalent state either by fusion with sodium peroxide or by treatment with nitric and perchloric acids. Hydrated tungsten trioxide is prevented from precipitating and interfering during titration by complexing soluble sodium tungstate, formed either by treatment of the sodium peroxide melt with water or after dissolution of tungsten trioxide in sodium hydroxide solution, with hydrofluoric acid[1]. Hydrofluoric acid also maintains titanium, zirconium, niobium, and tantalum in solution during the titration step, and eliminates interference from iron (III) in the sodium diphenylaminesulphonate end-point by forming a colourless ferric fluoride complex[1-4].

Interference from chromium (VI) is eliminated by reducing it to the trivalent state with ferrous ammonium sulphate. Vanadium (V) is also reduced by this reagent but is subsequently re-oxidized to the pentavalent state with potassium permanganate at room temperature; chromium (III) is not re-oxidized under these conditions[1-4]. Selenium, tellurium[3], and cerium are re-oxidized with potassium permanganate and cause high results for vanadium.

Up to approximately 50 mg of chromium (III), and moderate amounts of copper, cobalt, and nickel do not interfere in the detection of the end-point. Interference from cerium, and large amounts of copper, cobalt, and nickel is eliminated by separating these elements, and certain other elements (e.g., iron, titanium, zirconium, manganese, magnesium, cadmium, and some niobium and tantalum) from vanadium, as the hydrous oxides, by filtration of the aqueous solution of the sodium peroxide melt, and/or by precipitation of their hydrous oxides with sodium hydroxide[6,7]. During sample decomposition with acids, interference from 50 mg or more of chromium can be avoided by volatilizing it as chromyl chloride from a perchloric-hydrochloric acid medium, or by removing it by electrolysis with a mercury cathode.

Interference from large amounts of sodium salts, which are accumulated during the sodium hydroxide separation procedure, is avoided by separating the vanadium from the excess salts by precipitation as lead vanadate from an acetic acid medium[8]. Chromium is also separated from vanadium by this procedure, after reducing it to the trivalent state with hydrogen peroxide[8]. Selenium, tellurium, molybdenum, and tungsten are not separated from vanadium by either the sodium hydroxide or the lead vanadate separation procedures. Selenium, molybdenum, and tungsten co-precipitate as insoluble lead compounds with lead vanadate; tellurium is co-precipitated because of a similar reaction and/or because of the formation of hydrolysis compounds[9,10]. Moderate amounts of molybdenum and tungsten do not interfere in the separation of vanadium as lead vanadate. Large amounts of molybdenum may interfere.

In the method involving sample decomposition with acids, or after the dissolution of the lead vanadate precipitate, interference from selenium and tellurium can be eliminated, in the absence of hydrated tungsten trioxide, by separating these elements from vanadium by electrolysis with a mercury cathode in a perchloric or sulphuric acid medium, respectively[11]. In the presence of hydrated tungsten trioxide, interference from selenium, but not tellurium, can be eliminated by volatilizing it as the bromide from a hydrobromic-sulphuric acid medium[12].

Molybdenum (VI), arsenic (V), uranium (VI), beryllium, aluminum, manganese, zinc, and moderate amounts of phosphate do not interfere in the titration of vanadium[3].

Range

The method is suitable for samples containing approximately 0.1 to 60% of vanadium, but material containing higher concentrations can also be analyzed if a smaller sample, or a suitable aliquot of a solution of the sample is taken.

Reagents

Standard ferrous ammonium sulphate solution, 0.025 N. Dissolve 9.8038 g of ferrous ammonium sulphate hexahydrate in approximately 500 ml of oxygen-free water, add 50 ml of 50% sulphuric acid, and dilute to 1 litre with oxygen-free water.

Standard vanadium solution (1 ml = 2.5 mg of vanadium). Transfer 0.8926 g of pure vanadium pentoxide (Note 1) to a 250-ml beaker, add 20 ml of 10% sodium hydroxide solution, and heat gently until the oxide has dissolved. Dilute to approximately 75 ml with water and, using litmus paper, neutralize the solution approximately with 50% sulphuric acid. Add 10 ml in excess, and dilute the resulting solution to 200 ml with water.

Sodium diphenylaminesulphonate (oxidized) indicator tablets (0.001 g) or oxidized solution. Prepare the solution as described in the Volumetric-Stannous Chloride-Dichromate Method for total iron (p 276).

Ferrous ammonium sulphate solution, 8% w/v. Dissolve 8 g of ferrous ammonium sulphate hexahydrate in approximately 50 ml of water, add 5 ml of 50% sulphuric acid, and dilute to 100 ml with water. Prepare fresh as required.

Potassium permanganate solution, 1% w/v.

Sodium nitrite solution, 0.5% w/v. Prepare fresh as required.

Lead acetate solution, 10% w/v. Dissolve 10 g of lead acetate trihydrate $[Pb(CH_3COO)_2 \cdot 3H_2O]$ in water and dilute to 100 ml.

Sodium carbonate-potassium nitrate fusion mixture, 90% and 10% by weight, respectively.

Sulphuric acid, 50% and 1% v/v.

Nitric acid, 50% and 10% v/v.

Hydrochloric acid, 10% v/v.

Sodium hydroxide solutions, 50%, 10% and 2% w/v.

Acetic acid wash solution, 3% v/v.

Water (oxygen-free). Freshly boiled and cooled water.

Standardization of ferrous ammonium sulphate solution

Transfer a 10-20-ml aliquot of the standard vanadium solution to a 400-ml Teflon beaker (Note 2) and add 20 ml of 50% sulphuric acid. Dilute the solution to approximately 200 ml with water and allow it to cool to room temperature. While stirring, add 1% potassium permanganate solution, by drops, until a pink colour is obtained which persists for approximately 1 minute, then add 0.2-0.3 ml in excess, and allow the solution to stand for approximately 2 minutes to ensure the complete oxidation of the vanadium. Add 0.5% sodium nitrite solution (Note 3), by drops, until the purple colour of the permanganate ion is completely discharged, then add 4-5 drops in excess. Add 2 g of urea (Note 4), mix thoroughly, and allow the solution to stand for approximately 5 minutes to ensure the complete destruction of the excess nitrite. Add 3 ml of concentrated hydrofluoric acid (Note 5) and one sodium diphenylaminesulphonate indicator tablet (or 0.3 ml of oxidized solution). Allow the solution to stand for approximately 2 minutes to allow the complete development of the violet-blue indicator colour, then titrate the resulting solution with standard ferrous ammonium sulphate solution until the violet-blue colour has completely disappeared and the solution is pure green (Note 6).

Correct the result obtained by adding that obtained for an indicator blank (Notes 7 and 8). Determine the normality of the ferrous ammonium sulphate solution, and calculate the vanadium equivalent (mg/ml) (1 ml of 0.025 N ferrous ammonium sulphate solution = 1.274 mg of vanadium) (Note 9).

Alternatively, the ferrous ammonium sulphate solution can be standardized against a sample of ferrovanadium of known vanadium content, after decomposition of the sample, in a Teflon beaker, with sulphuric, hydrofluoric, and nitric acids, followed by evaporation of the solution to fumes of sulphur trioxide to remove excess hydrofluoric and nitric acids (Note 10). After dilution of the resulting solution to 200 ml with water, add sufficient 8% ferrous ammonium sulphate solution [as described in Procedure A(a)], if necessary, to reduce any chromium present, then proceed with the oxidation and subsequent titration of vanadium as described above. The vanadium equivalent of the ferrous ammonium sulphate solution can subsequently be determined by direct calculation.

Procedures

A - Large amounts of silica absent

(a) Cerium, selenium, tellurium, and large amounts of copper, nickel, cobalt and chromium absent

Transfer 0.1-1 g of powdered sample, containing up to approximately 60 mg of vanadium, to a 60-ml iron crucible, and add a four-fold weight excess of sodium peroxide. Mix thoroughly and cover the mixture with an additional 1 g of sodium peroxide. Cover the crucible with an iron cover, fuse the contents over a blast burner, and keep the melt at red heat for several minutes to ensure complete sample decomposition. Allow the melt to cool for approximately 5 minutes, then transfer the crucible and cover to a 600-ml (covered) Teflon beaker (Note 2) containing approximately 150 ml of water. When the subsequent reaction has ceased, remove the crucible and cover after washing them thoroughly with hot water, and boil the solution for approximately 10 minutes to destroy the residual peroxide. Using litmus paper, neutralize the solution approximately with 50% sulphuric acid and, if the sample contains tungsten, titanium, zirconium, niobium, and/or tantalum, add 5 ml of concentrated hydrofluoric acid (Note 11). Add 20 ml of 50% sulphuric acid in excess and cool the resulting solution to room temperature (Note 12).

By burette, add sufficient 8% ferrous ammonium sulphate solution to reduce any chromium (VI) present (Note 13), add 8-10 drops in excess, and mix thoroughly. While stirring, add 1% potassium permanganate solution from a burette until a pink colour is obtained which persists for approximately 1 minute, then add 0.2-0.3 ml in excess. Allow the solution to stand for approximately 2 minutes to ensure the complete oxidation of the vanadium (Note 14), then proceed with the reduction of the excess potassium permanganate with sodium nitrite solution, the destruction of the excess sodium nitrite with urea, and the subsequent titration of the vanadium as described above. Correct the result obtained for the sample by adding that obtained for the indicator blank (Note 7).

(b) Cerium and large amounts of copper, nickel, and/or cobalt present

Following sample decomposition by fusion with sodium peroxide and digestion of the melt in water as described above (Note 15), boil the solution for several minutes to coagulate the precipitate, and allow it to stand for approximately 15 minutes. Using a Buchner funnel and suction, filter the solution (Whatman No. 540 paper) (Note 16), and wash the beaker, paper, and precipitate thoroughly with hot 2% sodium hydroxide solution. Transfer the filtrate to a 600-ml Teflon beaker and, using litmus paper, neutralize the solution approximately with concentrated nitric acid. Add 2-3 ml in excess and evaporate the solution to approximately 100 ml.

Dissolve the precipitate with hot 10% nitric acid, and wash the paper and funnel thoroughly with the same solution followed by hot water. Discard the paper. Transfer the resulting solution to the beaker that contained the initial precipitate, and dilute to approximately 100 ml with water. Add

50% sodium hydroxide solution until the solution is almost neutral, heat to the boiling point and, while stirring, slowly pour the solution into a 600-ml beaker containing 100 ml of 10% sodium hydroxide solution. Boil the solution for several minutes, allow it to stand for approximately 15 minutes, then filter the solution as described above, and wash both beakers, the paper, and the precipitate thoroughly with 2% sodium hydroxide solution. Discard the paper and precipitate, and transfer the filtrate to the beaker containing the initial filtrate.

Using litmus paper, neutralize the combined solution approximately with concentrated nitric acid, add 0.5-1 ml in excess, and evaporate the solution to approximately 200 ml. Cool, add 10% sodium hydroxide solution until the solution is just alkaline, add 5-10 drops in excess, then add 30 ml of concentrated acetic acid. Add sufficient 30% hydrogen peroxide, by drops, to reduce any chromium (VI) present (Note 17), and boil the solution to remove excess hydrogen peroxide. While stirring, add sufficient 10% lead acetate solution to precipitate the vanadium as lead vanadate (Note 18), place the beaker on a steam-bath, and allow the solution to stand until the precipitate has settled (Note 19). Filter the solution (Whatman No. 42 paper) (Note 16) and wash the beaker, paper, and precipitate thoroughly with 3% acetic acid. Discard the filtrate.

Using a jet of hot water, transfer the precipitate, as quantitatively as possible, to the beaker in which the precipitation was carried out. Place the beaker under the funnel, and wash the paper thoroughly with hot 50% nitric acid to dissolve the remaining lead vanadate. Discard the paper. Wash down the sides of the beaker with hot 50% nitric acid (Note 20), then add 20 ml of 50% sulphuric acid, and evaporate the solution to fumes of sulphur trioxide (Notes 21 and 22). Cool, wash down the sides of the beaker with water, and evaporate the solution to fumes again to ensure the complete removal of nitric acid. Cool, add approximately 50 ml of water and heat gently to dissolve the soluble salts.

In the absence of tungsten, dilute the solution to approximately 200 ml with water, cool to room temperature, and proceed with the ferrous ammonium sulphate reduction step, if necessary (Note 23), the oxidation of vanadium, and the subsequent titration of vanadium as described in Procedure A(a).

In the presence of tungsten, cool the solution to room temperature, filter it (Whatman No. 42 paper) into a 600-ml Teflon beaker (Note 16), and wash the beaker, paper, and precipitate thoroughly with cold 1% sulphuric acid. Transfer the paper and precipitate to the beaker that initially contained the precipitate, and add 25 ml of water and 2 ml of 50% sodium hydroxide solution. Macerate the paper thoroughly with a glass rod, boil the solution for several minutes to dissolve the yellow hydrated tungsten trioxide, and digest the mixture on a hot-plate for approximately 10 minutes. Filter the solution (Whatman No 541 paper) into a 250-ml Teflon beaker, and wash the beaker, paper, and paper pulp residue thoroughly with hot water. Discard the paper and residue. Using litmus paper, neutralize the filtrate approximately with 50% sulphuric acid, add 5 ml of concentrated hydrofluoric acid, and add the resulting solution to the main solution containing the vanadium. Dilute the combined solution to approximately 200 ml with water, cool to room temperature, and proceed with the determination of vanadium as described above.

B - Large amounts of silica present

(a) Cerium and large amounts of copper, nickel, and/or cobalt absent

Transfer 0.1-1 g of powdered sample, containing up to approximately 60 mg of vanadium, to a 250-ml Teflon beaker, and moisten with several ml of water. Add 5 ml each of concentrated nitric and hydrochloric acids and 10 ml of concentrated hydrofluoric acid and allow the mixture to digest at room temperature for 15-20 minutes (Note 24). Add 20 ml of concentrated perchloric acid and evaporate the solution to fumes of perchloric acid. Cool, add 10 ml of water and 5 ml each of concentrated hydrochloric and hydrofluoric acids, and evaporate the solution to fumes again. Cool, add 50 ml of water, heat gently to dissolve the soluble salts, and filter the resulting solution (Whatman No. 40 paper) into a 600-ml Teflon beaker. Transfer the residue quantitatively to the filter paper, wash the beaker, paper, and residue with hot 10% hydrochloric acid, and then thoroughly with hot water to remove perchlorates.

Transfer the paper and contents to a 30-ml platinum crucible, burn off the paper at a low temperature, and ignite at approximately 750°C. Cool the crucible and fuse the residue with 1-2 g of 90% sodium carbonate-10% potassium nitrate fusion mixture. Allow the melt to cool and transfer the crucible and contents to the beaker (covered) containing the initial filtrate. When dissolution of the melt is complete, remove the crucible after washing it thoroughly with hot water, and evaporate the solution to fumes of perchloric acid.

Cover the beaker and, if more than approximately 50 mg of chromium (Note 25) are present, add concentrated hydrochloric acid in small increments, and evaporate the solution to fumes of perchloric acid after the addition of each increment until no further chromyl chloride (i.e., orange vapour) is expelled. Evaporate the resulting solution to 2-3 ml, or until the sodium and potassium salts begin to crystallize. Cool, wash down the sides of the beaker with water, add 30 ml of 50% sulphuric acid, and evaporate the solution to approximately 10 ml to ensure the complete removal of perchloric acid. Cool, add approximately 50 ml of water, heat gently to dissolve the soluble salts and, depending on the absence or presence of tungsten, proceed with the determination of vanadium as described in Procedure A(b).

(b) <u>Cerium and large amounts of copper, nickel, and/or cobalt present</u>

Following sample decomposition (Note 26), filtration of the solution (Note 27), and treatment of the acid-insoluble material as described above, evaporate the solution to approximately 5 ml (Note 28), cool, and dilute to 100 ml with water. Add 50% sodium hydroxide solution until the solution is almost neutral, heat to the boiling point, and proceed with the sodium hydroxide separation and filtration as described in Procedure A(b). Transfer the filtrate to a 600-ml beaker and, using litmus paper, neutralize the solution approximately with concentrated nitric acid. Add 2-3 ml in excess, and evaporate the solution to approximately 100 ml.

Dissolve the precipitate with hot 10% nitric acid, wash the paper and funnel thoroughly with the same solution, followed by hot water, and discard the paper. Transfer the resulting solution to the beaker that contained the initial precipitate and, if necessary, dilute to approximately 100 ml with water. Add 50% sodium hydroxide solution until the solution is almost neutral, and re-precipitate, filter, and wash the mixed hydrous oxide precipitate as described in Procedure A(b). Discard the paper and precipitate. Add the resulting filtrate to the initial filtrate, then proceed with the neutralization, acidification, and evaporation of the combined solution; the addition of sodium hydroxide solution and acetic acid; the reduction of chromium (VI) with hydrogen peroxide; the separation of vanadium as lead vanadate; and the subsequent determination of vanadium as described in Procedure A(b).

<u>Notes</u>

1. If the purity of the vanadium pentoxide is in doubt, the vanadium content of the reagent can be determined by titration with standard 0.1 N potassium permanganate solution, after the reduction of vanadium to the tetravalent state, as described in Note 1 (p 116) of the Spectrophotometric-N-Benzoyl-N-Phenylhydroxylamine Method for vanadium.

Then, the weight of vanadium pentoxide required for the standard solution

$$= 0.8926 \times \frac{56.01}{\text{Vanadium found (\%)}}$$

where:

56.01 = *the theoretical percentage of vanadium in pure vanadium pentoxide.*

If vanadium pentoxide is not available, ammonium metavanadate (NH_4VO_3) can be employed for the preparation of the standard vanadium solution, but the purity of this reagent should be determined as described in the above method.

2. A glass beaker can also be employed at this stage, but a Teflon beaker is preferable because etching of the glass will occur because of the reaction of hydrofluoric acid with the silica in the glass during the subsequent titration step.

3. Instead of sodium nitrite solution, approximately 0.65% sodium azide solution can be employed for the reduction of the excess potassium permanganate solution. However, the excess azide must be destroyed, prior to the titration of vanadium, by boiling the solution vigorously for about 10 minutes. The solution must subsequently be cooled to room temperature before the titration step[1,4].

4. Instead of urea, 5 ml of 10% sulphamic acid solution can be employed for the destruction of the excess sodium nitrite[3,4].

5. Instead of hydrofluoric acid, 5 or 10 ml of concentrated phosphoric acid can be employed for decolourizing the iron (III) that is produced during the subsequent titration step. However, hydrofluoric acid is recommended because it intensifies the sodium diphenylaminesulphonate indicator colour and sharpens the end-point. Hydrofluoric acid also eliminates interference from tungsten during the titration of vanadium in sample solutions prepared by the subsequent procedures[1-4]. Phosphoric acid cannot be employed to de-colourize iron (III) in the presence of tungsten, because a phosphovanadotungstic acid complex, which is only partly reduced by the iron (II) titrant, is formed and subsequently causes low results for vanadium[1].

6. A 20-ml portion of the vanadium solution (corrected for the indicator blank) (Note 7) requires 39.26 ml of 0.025 N ferrous ammonium sulphate solution.

7. Because sodium diphenylaminesulphonate is oxidized by vanadium (V), the result obtained will be low unless an indicator blank is determined and added to the result obtained. The indicator blank can be determined as follows[13]:

Treat an identical portion of the standard vanadium solution as described in the standardization procedure, but add 4 sodium diphenylaminesulphonate tablets (or 1.2 ml of oxidized solution), and titrate the solution as described.

Then, the amount "X" of vanadium (V) (in terms of the ferrous ammonium sulphate solution) required to oxidize the three additional indicator tablets (or the additional 0.9 ml of solution) $= V_1 - V_4$

where:

V_1 = *volume (ml) of ferrous ammonium sulphate solution required for the titration in the presence of one indicator tablet (or 0.3 ml of solution).*

V_4 = *volume (ml) of ferrous ammonium sulphate solution required for the titration in the presence of four indicator tablets (or 1.2 ml of solution).*

Consequently, the indicator blank, or the amount of vanadium (V) [in terms of the iron (II) solution] required to oxidize one sodium diphenylaminesulphonate tablet (or 0.3 ml of solution) is equivalent to $\frac{X}{3}$ ml of 0.025 N ferrous ammonium sulphate solution.

8. Ferroin (1,10-phenanthroline ferrous sulphate) can also be employed as internal indicator, but the sulphuric acid concentration of the solution should be adjusted to approximately 5 M prior to the titration step; at lower acidities the end-point appears too early. With this indicator (i.e., 1 drop of 0.025 M solution), the colour change at the end-point is from greenish-blue to reddish-green. The result obtained with this indicator should also be corrected by adding that obtained for an indicator blank determined as described in Note 7[14,15].

9. Because iron (II) solutions are susceptible to air-oxidation, the ferrous ammonium sulphate solution should be standardized daily just before use.

10. Any acid-insoluble material that is present at this stage should be quantitatively removed by filtration, ignited in a platinum crucible, and

fused with 1-2 g of sodium carbonate. The melt should subsequently be dissolved in the initial solution.

11. Additional hydrofluoric acid may be required to maintain tungsten, titanium, zirconium, niobium, and/or tantalum in solution, if the sample contains an appreciable amount of these elements.

12. The solution should not be warm during the subsequent reduction and oxidation steps or else chromium (III) may be partly oxidized to the hexavalent state during the oxidation of vanadium (IV) with potassium permanganate solution[4].

13. Complete reduction of chromium is indicated when the solution becomes clear green.

14. The reaction between vanadium (IV) and potassium permanganate is rapid in hot solutions but considerably slower at room temperature[4]. Consequently, the solution should be allowed to stand for several minutes after the addition of the excess potassium permanganate solution to ensure the complete oxidation of the vanadium.

15. A glass beaker can be employed for the digestion of the melt.

16. It is not necessary to transfer the precipitate quantitatively to the filter paper.

17. Complete reduction of chromium is indicated when the solution becomes clear green after it has been boiled to remove excess hydrogen peroxide. The solution will be brown initially because of the formation of the brown vanadium (V)-hydrogen peroxide complex.

18. Approximately 4 ml of 10% lead acetate solution are required for the precipitation of 60 mg of vanadium, but more will be required if molybdenum or soluble tungsten compounds are present at this stage. Both tungsten and molybdenum are precipitated, presumably as lead tungstate and lead molybdate, under the conditions employed for the precipitation of lead vanadate[10]. Complete separation of vanadium may not be obtained in the presence of an appreciable amount of molybdenum because the lead-molybdenum precipitate that is formed in acetic acid media tends to form a colloidal mixture that passes through the filter paper.

19. The lead vanadate precipitate is initially orange then fades to a white or yellowish-amber colour on standing.

20. Lead tungstate, if present in the precipitate, will not dissolve in the 50% nitric acid employed for the dissolution of the lead vanadate precipitate. This compound is converted to yellow hydrated tungsten trioxide, and lead is precipitated as the sulphate during the subsequent evaporation of the solution to fumes of sulphur trioxide.

21. If the sample contains selenium and/or tellurium, these elements will be present in the sample solution at this stage and will interfere in the subsequent determination of vanadium. Under the conditions employed for the precipitation of lead vanadate, selenium is co-precipitated as an insoluble lead-selenium compound that is soluble in the 50% nitric acid employed for the dissolution of the lead vanadate precipitate. Tellurium forms insoluble hydrolysis compounds and/or an insoluble lead-tellurium compound that is also soluble in 50% nitric acid. In the absence of hydrated tungsten trioxide, both selenium and tellurium can be separated from vanadium at this stage by electrolysis with a mercury cathode, as follows:

Evaporate the solution to approximately 5 ml, add 50 ml of water, and heat gently to dissolve the salts. Cool, transfer the solution to a mercury cathode cell, dilute to approximately 200 ml with water, and electrolyze the solution for 1 hour at approximately 10 amperes. Filter the electrolyte (Whatman No. 541 paper) into a 600-ml Teflon beaker and wash the cathode cell and paper with water. Discard the paper. Evaporate the solution to approximately 200 ml, add 10 ml of 50% sulphuric acid, cool the solution to room temperature, and proceed with the determination of vanadium as described.

Selenium and tellurium are not deposited in the mercury, but are quantitatively reduced to the elemental state during electrolysis and subsequently separated from vanadium during the filtration of the electrolyte[11]. In the presence of tungsten, prior removal of the hydrated tungsten trioxide by filtration is not recommended because the precipitate may occlude selenium and, particularly tellurium, which readily forms insoluble hydrolysis compounds in dilute acid media[9]. Some selenium and/or tellurium would subsequently be present in the final solution when the hydrated tungsten trioxide is treated as described in the subsequent procedure to recover the occluded vanadium.

22. If the sample contains selenium, but not tellurium, the selenium can be separated from vanadium at this stage, in the presence of hydrated tungsten trioxide, by volatilizing it as the bromide by the repeated addition of concentrated hydrobromic acid to the solution, followed by evaporation of the solution to fumes of sulphur trioxide. Tellurium is not separated from vanadium by this procedure[12].

23, If the sample contains chromium, the ferrous ammonium sulphate reduction step is recommended to avoid possible error resulting from any chromium (VI) that may not have been reduced during treatment of the solution with hydrogen peroxide prior to the precipitation of lead vanadate. Any un-reduced chromium (VI) would be co-precipitated as lead chromate with the lead vanadate precipitate[10]. If chromium is known to be absent, the reduction step can be omitted.

24. If lead, tungsten, and more than approximately 50 mg of chromium are absent, proceed as follows:

Add 30 ml of 50% sulphuric acid, instead of 20 ml of perchloric acid, and evaporate the solution to fumes of sulphur trioxide. Cool, add 10 ml of water and 5 ml each of concentrated hydrochloric and hydrofluoric acids, and evaporate the solution to fumes again. After filtration, ignition, and fusion of the acid-insoluble material, followed by dissolution of the melt in the initial filtrate, evaporate the solution to approximately 10 ml to remove hydrochloric acid and nitrate ion. Add 50 ml of water, heat to dissolve the soluble salts (Notes 22 and 25), then proceed with the determination of vanadium as described.

25. If tungsten is absent and selenium and tellurium are present, selenium, tellurium, and chromium can be separated from vanadium at this stage by electrolysis with a mercury cathode as described in Note 21. If sulphuric acid was employed for sample decomposition instead of perchloric acid (Note 24), proceed as described in Note 21, after filtration of the electrolyte. If perchloric acid was employed, proceed as described in the subsequent procedure. Iron, cobalt, nickel, copper, and lead are also separated from vanadium by this procedure[11].

If selenium alone is present, it can be separated from vanadium by volatilization as the bromide as described in Note 22, after the separation of chromium by volatilization as chromyl chloride, and the subsequent removal of the perchloric acid by evaporation with sulphuric acid.

26. In this procedure, sulphuric acid (Note 24) cannot be employed for sample decomposition because lead will precipitate as the insoluble sulphate, rather than lead vanadate, during the subsequent separation of vanadium as lead vanadate.

27. A glass beaker can be employed for the collection of the filtrate.

28. If hydrated tungsten trioxide is absent, selenium and/or tellurium, if present, should be removed at this stage by a mercury cathode separation as described in Note 21.

Calculations

Normality of ferrous ammonium sulphate solution $[N_{Fe(II)}]$

$$= \frac{\text{Weight of vanadium in aliquot taken (g)}}{0.05094 \times (V + v)}$$

where:

V = volume (ml) of ferrous ammonium sulphate solution required for the vanadium.

v = volume (ml) of ferrous ammonium sulphate solution required for the indicator blank.

Vanadium equivalent (mg/ml) of the ferrous ammonium sulphate solution (V_{EQ}) = $N_{Fe(II)} \times 50.94$ OR

$$= \frac{\text{Weight of vanadium in aliquot taken (mg)}}{V + v}$$

where:

V and v are as described above.

$$\% \; V = \frac{(V_S + v) \times V_{EQ}}{\text{Sample weight (mg)}} \times 100$$

where:

V_S = volume (ml) of ferrous ammonium sulphate solution required for the sample.

v is as described above.

$\% \; V_2O_5 = 1.785 \times \% \; V$

$\% \; V_2O_3 = 1.471 \times \% \; V$

Other applications

With suitable modifications in the decomposition procedure, the method described in Procedure B(a) can be employed to determine vanadium in iron and steel[1-3].

References

1. H.H. Willard and P. Young, Ind. Eng. Chem., Anal. Ed., 4, 187 (1932).
2. Idem, ibid., 5, 158 (1933).
3. E.C. Pigott, "Ferrous Analysis - Modern Practice and Theory", 2nd ed., Chapman and Hall, Ltd., London, pp 524-531 (1953).
4. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 8, pp 222-228, 264 (1963).
5. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, 1208 (1962).
6. I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry", Interscience, New York, Part II, vol. 8, pp 205-206 (1963).
7. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 81-83 (1938).
8. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, pp 1209-1211 (1962).
9. Idem, ibid., 946 (1962).
10. W.F. Hillebrand, G.E.F. Lundell, H.A. Bright and J.I. Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 456, 327 (1953).
11. G.E.F. Lundell and J.I. Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Sons, Inc., New York, pp 94-95 (1938).
12. N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 6th ed., D. Van Nostrand Company, Inc., New York, vol. 1, 928 (1962).
13. Idem, Ind. Eng. Chem., 17, 314 (1925).
14. I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience Publishers, Inc , New York, vol. III, 607 (1957).
15. G.H. Walden, Jr., L.P. Hammett and S.M. Edmonds, J. Am. Chem. Soc., 56, 57 (1934).

APPENDIX

TABLE I

Common Acids and Alkalies - Useful Data

	HCl	HNO_3	HF	$HClO_4$	H_2SO_4	H_3PO_4	CH_3COOH	NH_4OH
Molecular Weight	36.46	63.02	20.01	100.46	98.07	98.00	60.03	35.04
Average specific gravity of concentrated reagent	1.19	1.42	1.15	1.68	1.84	1.69	1.06	0.90
Average % present in concentrated reagent	36.0	69.5	48.0	71.0	96.0	85.0	99.5	58.6
Gms "active" ingredient per ml	0.426	0.985	0.552	1.19	1.77	1.44	1.055	0.527
Normality of concentrated reagent	11.7	15.6	27.6	11.8	36.1	44.0	17.6	15.1
Molarity of concentrated reagent	11.7	15.6	27.6	11.8	18.0	14.7	17.6	15.1
Ml concentrated reagent per litre of <u>IN</u> solution	85.5	64.0	36.2	84.4	27.8	22.7	56.9	66.5
Ml concentrated reagent per litre of <u>1M</u> solution	85.5	64.0	36.2	84.4	55.6	68.2	56.9	66.5

TABLE II

International Atomic Weights (1963)

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	(227)	Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	(243)	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	(237)
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	(210)	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	(249)	Nobelium	No	102	(254)
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	(242)
Californium	Cf	98	(251)	Polonium	Po	84	(210)
Carbon	C	6	12.01115	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132.905	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.453	Protactinium	Pa	91	(231)
Chromium	Cr	24	51.996	Radium	Ra	88	(226)
Cobalt	Co	27	58.9332	Radon	Rn	86	(222)
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	(247)	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteintium	Es	99	(254)	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100	(253)	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	(223)	Silver	Ag	47	107.870
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulphur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	(99)
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lw	103	(257)	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutecium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	(256)				