SOME INSTRUMENTAL METHODS FOR THE DETERMINATION OF MINOR AND TRACE ELEMENTS IN IRON, STEEL AND NON-FERROUS METALS AND ALLOYS

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PREFACE

The instrumental methods described in this book were developed by the author during approximately twenty years of research and development work involving the determination of trace and minor elements in ores, metals and alloys. The methods for determining impurities in high-purity molybdenum and tungsten metals were developed during early collaborative work carried out by the Analytical Chemistry Subdivision of the former Mineral Sciences Division in cooperation with the Specialist Group of Refractory Metals Analysis of the Structures and Materials Group of the Advisory Group for Aerospace Research and Development (AGARD) of NATO. Various methods for determining trace and minor elements in copper-base alloys were developed during collaborative work with the National Bureau of standards in Washington, D.C. on the analysis of brasses and bronzes for use as spectrographic standards. Many of the more recent methods were developed primarily for use in the analysis of candidate reference ores and concentrates produced by the Canadian Certified Reference Materials Project (CCRMP) sponsored by CANMET. However, during the course of the experimental investigation work on these methods, many of them were also applied to iron and steel and to various non-ferrous materials. Most of these methods are scattered throughout Talanta, and some are briefly described in old obscure Mines Branch test reports. Consequently, it was considered that a collection of these methods in book form would be of value in the present Mineral Sciences Laboratories Chemical Laboratory and in many industrial and commercial laboratories.

In this book, an attempt has been made to provide a comprehensive account of the procedure or procedures used for the analysis of each element and to furnish chemists and other workers with information on the chemical reactions involved, on pertinent interferences and on the limitations of the method. Care has been taken to set forth the steps of each procedure in a logical sequence and to clarify the reason for each step to emphasize the importance of details which, if omitted, could lead to incorrect results. No claim is made that a particular method will be applicable to all the types of steel or to the different types of a particular alloy that can be encountered in the chemical laboratory. However, the decomposition procedures described and the subsequent instrumental finishes are applicable to the types of sample materials listed in the appropriate table in Appendix A. These tables, except as indicated in Tables 22 and 23, show the results obtained by the author, during preliminary experimental work, for National Bureau of Standards, British Chemical Standards and CCRMP certified reference materials and, where reference

materials were not available, for materials to which known amounts of the desired element were added. It is considered that these results may be of value, for comparison purposes, to chemists using these methods. They also show the accuracy and, in some instances, the precision attainable by the methods.

Although rapid atomic-absorption spectrophotometric (AAS) methods have replaced many spectrophotometric methods, particularly for the determination of aluminum, copper, iron, manganese and nickel, spectrophotometric methods for these elements have been included in this book because they are still of value in umpire work and to laboratories without AAS facilities. The experimental work in all the recently published AAS methods was carried out with a Varian Techtron Model AA 6 spectrophotometer. Methods for the determination of impurities in high-purity niobium and tantalum metals, which were developed at the same time as those for high-purity molybdenum and tungsten metals, have not been included because they are considered to be of limited interest to analysts. References to these methods can, in most cases, be found at the end of the account of the particular method for high-purity molybdenum and tungsten metals.

The concentrations of ammonium hydroxide and all concentrated acids used in these methods are those shown in Table 1 in Appendix B. Unless otherwise specified, distilled water should be used to prepare dilute solutions of these reagents and of all solid reagents. In the spectrophotometric methods, the exact recommended volume of the complex-forming or chromogenic reagent should be added to the calibration and sample solutions.

An effort has been made throughout this collection of methods to conform to current SI usage according to the Canadian Metric Practice Guide. However, in the interest of brevity, the non SI symbol "M" is used to denote concentration in moles per litre.

Special thanks are due to D.M. Varette for typing the original drafts of the methods and the tables and to L. Hosson of the Word Processing Unit for typing this report.

Ottawa, Canada
August 1980

Elsie M. Donaldson

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ATOMIC-ABSORPTION DETERMINATION OF ALUMINUM IN IRON, STEEL, FERROVANADIUM AND COPPER- AND NICKEL-BASE ALLOYS AFTER A MERCURY CATHODE SEPARATION AND EXTRACTION OF THE ALUMINUM ACETYLACETONE COMPLEX

PRINCIPLE

Matrix elements are separated from aluminum by electrolysis with a mercury cathode in a 2-3% perchloric or sulphuric acid medium and aluminum is subsequently separated from phosphate and other elements by chloroform extraction of its acetylacetone complex from a weakly acidic - pH 6.5 - ammonium acetate-hydrogen peroxide medium. Aluminum is ultimately determined by atomic-absorption spectrophotometry at 309.3 nm in a strongly reducing nitrous oxide-acetylene flame in a 5% perchloric acid medium containing 1000 µg/mL of sodium as the chloride (1).

INTERFERENCES

Large amounts of iron, chromium, nickel, titanium, vanadium and cobalt interfere in the determination of aluminum in a nitrous oxide-acetylene flame (2-4). In this method, iron, chromium, nickel, cobalt and various other elements - copper, zinc, molybdenum, tin, bismuth, lead and some manganese - are separated from aluminum by electrolysis with a mercury cathode in a dilute perchloric or sulphuric acid medium. Aluminum is subsequently separated from titanium, vanadium and phosphate, and from any residual nickel, cobalt, molybdenum and manganese by chloroform extraction of its acetylacetone complex from a weakly acidic, 0.1 M acetylacetone-ammonium acetate medium containing hydrogen peroxide as a complexing agent for titanium, vanadium, molybdenum and tungsten. Residual iron and copper are completely coextracted as acetylacetone complexes, but up to at least 10 mg of iron and 5 mg of copper can be present during the extraction step without interfering in the extraction of up to 2 mg of aluminum or in the subsequent atomic-absorption determination of aluminum under the recommended conditions (1). Residual chromium, which is reduced to chromium (III) with hydrogen peroxide in an acid medium, is slightly coextracted (5). However, up to at least 10 mg of chromium (III) can be present during the extraction step without causing error in the aluminum result (1).

Up to at least 10 mg each of cobalt, nickel and phosphorus (V) - as orthophosphate - and up to at least 20 mg each of molybdenum (VI), tungsten (VI), manganese (II) and titanium (IV) can be present during the extraction step without interfering in the extraction of aluminum (1). Up to 5 mg each of cerium (IV), lead, niobium and tantalum also do not interfere (5). Up to at least 150 mg of vanadium (V) can be present during the extraction of aluminum if sufficient hydrogen peroxide is added to complex it and prevent its coextraction (1).

Possible interference from perchloric acid during the atomic-absorption determination of aluminum is avoided by maintaining approximately the same concentration - 5% by volume - in the sample and calibration solutions. Ionization of aluminum is suppressed by adding approximately 1000 µg/mL of sodium - as the chloride - to both the sample and the calibration solutions (1).

RANGE

This method is suitable for iron, steel and copper- and nickel-base alloys containing approximately 0.0005 to 2% of aluminum and for ferrovanadium containing approximately 0.001 to 2%.

APPARATUS

MERCURY CATHODE.

REAGENTS

STANDARD ALUMINUM SOLUTION, 1000 µg/mL. Transfer 1.0000 g of high-purity aluminum metal and about

5 mg of high-purity iron metal (Note 1) to a 400-mL beaker and add 20 mL of concentrated hydrochloric acid. Cover the beaker and heat the mixture gently until the aluminum and iron have dissolved, then cool the solution to room temperature, transfer it to a 1-L volumetric flask and dilute it to volume with water. Store the resulting solution in a plastic bottle. Prepare a 100-µg/mL solution by diluting 20 mL of this stock solution to 200 mL with water. Prepare the diluted solution fresh as required.

ACETYLACETONE SOLUTION, 20% *V/V*. Transfer 20 mL of 2, 4-pentanedione to a 100-mL volumetric flask containing 30 mL of ethyl alcohol and dilute the solution to volume with water. This solution is stable for at least one week.

SODIUM SOLUTION, 10 000 µg/mL. Dissolve 12.7 g of sodium chloride in water and dilute the solution to 500 mL. Store the solution in a plastic bottle.

AMMONIUM ACETATE SOLUTION, 50% *m/v*.

SULPHURIC ACID, 1 and 50% *V/V*.

PERCHLORIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION SOLUTIONS

Add 10 mL each of 50% perchloric acid and 10 000-µg/mL sodium solution to each of nine 100-mL volumetric flasks; then by burette, add to the first eight flasks, 1, 2, 3, 5, 10, 15, 20 and 25 mL, respectively, of the dilute standard 100-µg/mL aluminum solution. The contents of the last flask constitute the zero calibration solution. Dilute each solution to volume with water (Note 2).

PROCEDURES

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

A - Iron, steel and nickel-chromium alloys

Transfer 0.1-1 g of sample (Note 3) containing not more than 2 mg of aluminum to a 400-mL beaker, then cover the beaker and add 15 mL of concentrated hydrochloric acid and 5 mL of concentrated nitric acid. Heat the mixture until the sample has dissolved, then add 20 mL of concentrated perchloric acid (Note 4) and evaporate the solution to fumes of perchloric acid. Remove the cover and carefully evaporate the solution to 5-7 mL. Cool the solution to room temperature, add 50 mL of water and heat the solution gently to dissolve the salts. Add about one-quarter of a Whatman filter pulp tablet, macerate it with a stirring rod, then using Whatman No. 40 paper, filter the solution into a 400-mL beaker and transfer the residue quantitatively to the filter paper. Wash the paper and the residue 3 times with water, then wash them 3 times with 1% sulphuric acid to ensure the complete removal of perchloric acid. Evaporate the filtrate to about 75 mL (Note 5).

Transfer the paper containing the residue to a 30-mL platinum crucible, burn off the paper at a low temperature and ignite the residue at 600-700°C. Cool the crucible and add 1 mL each of 50% sulphuric acid and concentrated nitric (Note 6) and hydrofluoric acids. Heat the mixture gently to dissolve the residue, then evaporate the solution to dryness. Fuse the resulting residue with 2 g of fused sodium hydrogen sulphate (Note 7), then cool the crucible and transfer it to a 250-mL beaker containing about 50 mL of water. Cover the beaker and heat the solution gently to dissolve the melt. Remove the crucible after washing it thoroughly with water (Note 8), then add the solution to the initial filtrate.

Transfer the resulting solution to a mercury cathode cell, dilute it to about 200 mL with water and electrolyze the solution for 75 min at approximately 10 A. Using Whatman No. 541 paper, filter the electrolyte into the 400-mL beaker that initially contained the solution. Wash the cathode cell and the paper thoroughly with water, then discard the paper. Add 5 mL of concentrated

hydrochloric acid and 3 mL of 50% sulphuric acid to the filtrate and evaporate the solution until 1.5-2 mL of sulphuric acid remains (Note 9). Cool the beaker and add 50 mL of water. Heat the solution gently until it is clear (Note 10), then cool it to room temperature.

In succession, add 2 mL of 30% hydrogen peroxide, 5 mL of 20% acetylacetone solution and 10 mL of 50% ammonium acetate solution to the resulting solution, then using a pH meter, adjust the pH of the solution to 6.5 ± 0.1 with concentrated ammonium hydroxide. Transfer the solution to a 125-mL separatory funnel, add 10 mL of chloroform, close the funnel and shake it for 2 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 100-mL beaker. Extract the aqueous phase two more times by shaking it for 1 min each time with 5 mL of chloroform, then wash it by shaking it for about 30 s with 5 mL of chloroform. Add 5 drops of concentrated hydrochloric acid to the combined extracts, then evaporate the mixture to dryness in a hot water-bath. Add 1 mL of 50% perchloric acid and 2 mL of concentrated nitric acid to the residue in the beaker, cover the beaker and heat the solution until fumes of perchloric acid are evolved (Note 11). Cool the solution to room temperature and add about 3 mL of water. Transfer the blank solution to a 10-mL volumetric flask containing 1 mL of 10 000-µg/mL sodium solution. Depending on the expected aluminum content, transfer the sample solution to a volumetric flask of appropriate size - 10-100 mL - and add sufficient 10 000-µg/mL sodium solution so that 1 mL will be present for each 10 mL of final solution. If necessary, add sufficient 50% perchloric acid so that 1 mL will be present for each 10 mL of final solution in excess of 10 mL (Note 12). Dilute each solution to volume with water.

Measure the absorbance of the resulting solutions at 309.3 nm in a strongly reducing nitrous oxide-acetylene flame (Note 13). Determine the aluminum contents, in milligrams, of the solutions by relating the resulting values to those obtained concurrently for calibration solutions of slightly higher and lower aluminum concentrations. Correct the result obtained for the sample solution by subtracting that obtained for the reagent blank solution.

B - Ferrovanadium

Decompose 0.1-0.5 g of sample containing up to 2 mg of aluminum as described in Procedure A, using 20 mL of 50% sulphuric acid instead of concentrated perchloric acid. Heat the solution until the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution to 5-7 mL. Cool the solution and add 50 mL of water. Heat the solution to dissolve the salts, then proceed with the filtration of the solution (Note 14), the treatment of the residue, the mercury cathode separation (Note 15), the extraction (Note 16) and the subsequent determination of aluminum as described in Procedure A.

C - Copper-base and nickel-copper alloys

Transfer 0.1-1 g of sample containing up to 2 mg of aluminum to a 400-mL beaker (Note 17), then cover the beaker and add 5 mL each of water and concentrated nitric acid and 20 mL of 50% sulphuric acid. Heat the mixture until the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution to 5-7 mL. Cool the solution and add 50 mL of water. If necessary, heat the solution to dissolve the salts, transfer it to a mercury cathode cell, dilute it to 200 mL with water and proceed with the mercury cathode separation (Note 15), the extraction and the subsequent determination of aluminum as described in Procedure A.

NOTES

1. Iron hastens the dissolution of the aluminum metal.
2. The calibration solutions should be prepared fresh every week.
3. More than 1 g of sample is not recommended because too much iron may remain in the solution after the mercury cathode separation step. The residual iron is coextracted and,

if a large amount is present, may result in an explosive reaction when the final solution is evaporated to fumes of perchloric acid. Too much iron can also cause a slight positive error in the aluminum result.

4. For iron and steel of low chromium content and high titanium, vanadium, molybdenum or tungsten content, add 20 mL of 50% sulphuric acid instead of perchloric acid and proceed as described in Procedure B.
5. If the acid-soluble aluminum content of the sample is required, proceed with the mercury cathode separation, the extraction and the subsequent determination of aluminum as described.
6. Nitric acid is added to dissolve any elemental silicon present.
7. One gram of a mixture consisting of 75% by mass of sodium carbonate and 25% by mass of fused boric acid - i.e., boron trioxide - can also be used for fusion of the insoluble material. If this mixture is used, the melt should be dissolved in water containing 2 mL of 50% sulphuric acid.
8. If the aluminum content of the acid-insoluble material is required, it can be determined in the resulting solution. In this case, omit the mercury cathode separation, add the volumes of hydrogen peroxide, acetylacetone and ammonium acetate solutions recommended in the subsequent part of the procedure and proceed with the pH adjustment, the extraction and the determination of aluminum as described. The total amount of aluminum present in the sample can then be determined by adding that found in the acid-insoluble material to that found in the filtrate (Note 5).

   The separate determination of the acid-insoluble aluminum is recommended if appreciable tungsten trioxide is present in the acid-insoluble material. In this case, add 5 mL of 30% hydrogen peroxide and the recommended volumes of acetylacetone and ammonium acetate solutions to the solution obtained after dissolving the melt, then add sufficient concentrated ammonium hydroxide to dissolve the tungsten trioxide. Acidify the solution with 50% sulphuric acid, adjust the pH to 6.5 ± 0.1 and proceed with the extraction and subsequent determination of aluminum.
9. Sulphuric acid solutions of aluminum should not be evaporated to dryness. This results in the formation of an anhydrous aluminum sulphate that is virtually insoluble in water or in dilute acid. This causes a low result for aluminum (6).
10. Some flocculent silica - originally present as soluble silica in the initial filtrate - may be present at this stage but it does not interfere in the subsequent extraction step. If the extraction cannot be completed the same day, allow the solution to stand overnight at this point.
11. The solution should not be allowed to evaporate to dryness. If the atomic-absorption determination cannot be completed the same day, allow the solution to stand overnight at this point. The final aluminum solution is not stable on prolonged standing.
12. Additional 50% perchloric acid is not required if the final volume of the solution is to be 10 mL because 1 mL is added to the residue remaining after the removal of chloroform. For final sample solution volumes of 25, 50 or 100 mL, add 1.5, 4 or 9 mL, respectively.
13. A strongly reducing, non-luminous nitrous oxide-acetylene flame is required to obtain the highest sensitivity for aluminum. The height at which the beam from the hollow-cathode lamp passes through the flame is also extremely important (2,3). Consequently, after all other instrumental parameters have been set, the acetylene and nitrous oxide flow-rates should be adjusted to give the maximum "red feather" - 15-20 mm - without producing a luminous flame. Under these conditions, very little carbon is deposited in the burner slot. Subsequently, the height of the burner should be adjusted to give maximum absorbance while a solution containing aluminum is aspirated into the flame.

About five- to ten-fold scale expansion is recommended for the determination of aluminum.

14. It is not necessary to wash the paper and residue with 1% sulphuric acid as described in Procedure A.
15. It is not necessary to add 3 mL of 50% sulphuric acid after the mercury cathode separation.
16. More than 2 mL of 30% hydrogen peroxide - as recommended in Procedure A - will be required for samples of high vanadium content. Approximately 1 mL is required to complex 30 mg of vanadium. Five mL should be added for a 0.5-g sample of ferrovanadium containing about 30% of vanadium. The solution should be yellow - not green - after the pH adjustment.
17. If the sample contains silicon, use a 400-mL teflon beaker and add 1 or 2 mL of concentrated hydrofluoric acid during the decomposition step.

ACCURACY

Illustrated in Table 1 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine aluminum in tin-, zinc- and cobalt-base alloys and in nickel oxide.

REFERENCES

1. Donaldson, E.M. "Determination of aluminium in iron, steel and ferrous and non-ferrous alloys by atomic-absorption spectrophotometry after a mercury cathode separation and extraction of the aluminum acetylacetone complex"; Talanta 28:461-467; 1981.

2. Marks, J.Y. and Welcher, G.G. "Interelement interferences in atomic absorption analyses with the nitrous oxide-acetylene flame"; Anal Chem 42:1033-1040; 1970.

3. Amos, M.D. and Thomas, P.E. "The determination of aluminum in aqueous solution by atomic-absorption spectroscopy"; Anal Chim Acta 32:139-147; 1965.

4. Konig, P., Schmitz, K.-H and Thiemann, E. "Determination of aluminum in low and high alloy steels, in ores and slags by atomic absorption spectrometry"; Z Anal Chem 244:232-235; 1969.

5. Donaldson, E.M. "Determination of aluminum in molybdenum and tungsten metals, iron, steel and ferrous and non-ferrous alloys with pyrocatechol violet"; Talanta 18:905-915; 1971.

6. Kolthoff, I.M. and Elving, P.J. "Treatise on analytical chemistry" (Part II); New York, Interscience; 4:377; 1966.

SPECTROPHOTOMETRIC DETERMINATION OF ALUMINUM IN IRON, STEEL, FERROVANADIUM, COPPER- AND NICKEL-BASE ALLOYS AND MOLYBDENUM AND TUNGSTEN METALS WITH PYROCATECHOL VIOLET

PRINCIPLE

Matrix elements are separated from aluminum - if necessary - by electrolysis with a mercury cathode in a 2-2.5% sulphuric acid medium and aluminum is subsequently separated from phosphate and other elements by chloroform extraction of its acetylacetone complex from a weakly acidic - pH 6.5 - ammonium acetate-hydrogen peroxide medium. Aluminum is back-extracted into concentrated hydrochloric acid, and iron and other residual elements are subsequently separated from aluminum by a combined ammonium pyrrolidinedithiocarbamate-cupferron-chloroform extraction from a 10% hydrochloric acid medium. Aluminum is ultimately determined spectrophotometrically by measuring the absorbance at 578 nm of the red 1:2 aluminum-pyrocatechol violet complex formed at pH 6.10 in an ammonium acetate medium. The molar absorptivity of the complex at this wavelength is 7.03×10^3 $L.mol^{-1}.mm^{-1}$ (1,2).

INTERFERENCES

Numerous elements, including iron (III), iron (II), copper (II), chromium (III), chromium (VI), beryllium, molybdenum (VI) and tungsten (VI) interfere in the determination of aluminum because they also form coloured complexes with pyrocatechol violet (3-8). Interference from large amounts of iron, and from copper, zinc, nickel and chromium is avoided to a large extent by separating the bulk of these elements from aluminum by electrolysis with a mercury cathode. Interference from up to at least 4 mg of phosphorus (V) - as orthophosphate - and from up to at least 5 mg of cerium (IV), manganese (II), nickel, zinc, thorium (IV), titanium (IV), vanadium (V), niobium (V) and tantalum (V) is eliminated by separating aluminum from these elements by chloroform extraction of its acetylacetone complex at pH 6.5 from a 0.05 M acetylacetone-ammonium acetate-hydrogen peroxide medium. The presence of hydrogen peroxide during the extraction step eliminates interference from up to approximately 500 mg of molybdenum or tungsten (1). It also complexes and prevents the coextraction of vanadium (9) and keeps niobium, tantalum and titanium in solution during the extraction step. Cerium (IV) and thorium (IV) form hydrous oxides during the pH adjustment step, but the precipitates float on top of the chloroform phase and do not interfere with the extraction of aluminum. Zirconium, in microgram quantities, interferes because it causes emulsification in the chloroform phase (1).

Beryllium and small amounts of iron (III) and copper (II) that remain in the electrolyte after the mercury cathode separation step are completely extracted as acetylacetone complexes under the conditions used for the extraction of aluminum. Molybdenum (VI), chromium (III), cobalt (II) and lead are coextracted to a slight extent. Interference from this residual iron, molybdenum, cobalt and lead is eliminated by separating them from aluminum by a combined ammonium pyrrolidine-dithiocarbamate-cupferron-chloroform extraction from a 10% hydrochloric acid medium. Beryllium and chromium do not form pyrrolidine-dithiocarbamate or cupferron complexes and copper is not completely separated from aluminum under these conditions. Interference from residual copper (II) - microgram quantities - is eliminated by reducing it to the cuprous state with ascorbic acid before the formation of the aluminum-pyrocatechol violet complex. Beryllium, in amounts approximately equal to the amount of aluminum present, does not cause significant error in the result. More than about 2 mg of chromium (III) may interfere with the extraction of the aluminum-acetylacetone complex from a 0.05 M acetylacetone medium (1). Chromium (III) and chromium (VI) also interfere during complex formation because of the slow for-

mation of a pyrocatechol violet complex at room temperature. Chromium (VI) is reduced to chromium (III) during complex formation with pyrocatechol violet (8). Initially, the formation of the aluminum complex is inhibited in solutions containing chromium. However, the absorbance of these solutions increases on standing. Reasonably accurate results can be obtained in the presence of up to approximately 20 µg of chromium in the final aliquot taken for analysis if the absorbance is measured 15-30 min after the pH adjustment. However, if necessary, coextracted chromium can be readily removed from the final solution by volatilizing it as chromyl chloride from a hydrochloric acid-perchloric acid medium (1).

RANGE

This method is suitable for molybdenum and tungsten metal containing approximately 0.001 to 0.2% of aluminum and for iron, steel, ferrovanadium and copper- and nickel-base alloys containing up to approximately 1%.

APPARATUS

MERCURY CATHODE.

REAGENTS

STANDARD ALUMINUM SOLUTION, 0.5 mg/mL. Dissolve 0.5000 g of high-purity aluminum metal by heating it with 50 mL of 50% sulphuric acid. Cool the solution to room temperature, dilute it to 1 L with water and store it in a plastic bottle. Prepare a 5-µg/mL solution by diluting 5 mL of this stock solution to 500 mL with water. Prepare the diluted solution fresh as required.

PYROCATECHOL VIOLET SOLUTION, 0.08% *m/V*. Dissolve 0.2000 g of pyrocatecholsulphonphthalein in water and dilute the solution to 250 mL (Note 1).

ACETYLACETONE SOLUTION, 10% *V/V*. Transfer 5 mL of 2,4-pentanedione to a 50-mL volumetric flask containing 10 mL of ethyl alcohol and dilute the solution to volume with water. This solution is stable for at least one week.

AMMONIUM ACETATE BUFFER SOLUTION, 1.3 M. Dissolve 100 g of the reagent in water and dilute the solution to approximately 1 L, then using a pH meter, adjust the pH of the solution to 6.10 ± 0.03 with concentrated acetic acid (Note 2).

ASCORBIC ACID SOLUTION, 5% *m/V*. Prepare a fresh solution every two days.

AMMONIUM PYRROLIDINEDITHIOCARBAMATE-CUPFERRON SOLUTION, 1% and 3% *m/V*, respectively. Prepare the solution fresh as required and filter it before use.

AMMONIUM ACETATE SOLUTION, 50% *m/V*.

AMMONIUM HYDROXIDE, 10% *V/V*.

SULPHURIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION CURVE

Add 0.2 mL of 50% sulphuric acid to each of six 100-mL beakers; then by burette, add to the last five beakers 1, 2, 4, 6 and 8 mL, respectively, of the dilute standard 5-µg/mL aluminum solution and dilute each solution to approximately 20 mL with water. The contents of the first beaker constitute the blank. Add 2 mL of 5% ascorbic acid solution, 4 mL of 0.08% pyrocatechol violet solution and 1 mL of 50% ammonium acetate solution to each beaker, then using a pH meter, adjust the pH of each of the resulting solutions to 6.10 ± 0.03 with concentrated ammonium hydroxide and with 10% ammonium hydroxide. Add 5 mL of 1.3 M ammonium acetate buffer solution, then transfer each solution to a 100-mL volumetric flask and dilute it to volume with water. Measure the absorbance of each solution at 578 nm against water as the reference solution, using 10-mm cells. Correct the absorbance value obtained for each aluminum-pyrocatechol violet solution by subtracting that obtained for the blank solution. Plot micrograms of aluminum vs absorbance.

PROCEDURES

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

A - Iron, ferrovanadium and steel

Transfer 0.2-2 g of sample containing not more than 2 mg of aluminum to a 250-mL beaker (Note 3) and add 30 mL of water and 15 mL of 50% sulphuric acid. Cover the beaker and heat the mixture until the sample has dissolved (Note 4). Using Whatman No. 40 paper, filter the solution into a 200-mL volumetric flask and wash the beaker and the paper and residue each several times with water. Retain the beaker.

Transfer the paper containing the residue to a 30-mL platinum crucible, burn off the paper at a low temperature and ignite the residue at 600-700°C. Cool the crucible and add 1 mL each of 50% sulphuric acid and concentrated hydrofluoric and nitric acids (Note 5). Heat the mixture gently to dissolve the residue, then evaporate the solution to dryness. Fuse the residue with 2 g of potassium pyrosulphate, then cool the crucible and transfer it to the original beaker. Add about 50 mL of water and 5 mL of 50% sulphuric acid, heat the solution gently to dissolve the melt, then remove the crucible after washing it thoroughly with water (Note 6). Add the resulting solution (Note 7) to the initial filtrate and dilute the solution to volume with water (Note 8).

Transfer a 50-mL aliquot of the resulting solution to a mercury cathode cell, dilute it to about 100 mL with water and electrolyze the solution for 1 h at approximately 10 A. Using Whatman No. 541 paper, filter the electrolyte into a 250-mL beaker and wash the cathode cell and the paper thoroughly with water. Discard the paper. Add 5 mL of concentrated hydrochloric acid to the filtrate and evaporate the solution until 1.5-2 mL of sulphuric acid remains (Note 9). Cool the beaker and add 50 mL of water. Heat the solution gently until it is clear (Note 10), then cool it to room temperature.

In succession, add 2 mL of 30% hydrogen peroxide (Note 11), 5 mL of 10% acetylacetone solution and 10 mL of 50% ammonium acetate solution to the resulting solution, then using a pH meter, adjust the pH of the solution to 6.5 ± 0.1 with concentrated ammonium hydroxide. Transfer the solution to a 125-mL separatory funnel, add 10 mL of chloroform, close the funnel and shake it for 2 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-mL separatory funnel. Extract the aqueous phase two more times by shaking it for 1 min each time with 5 mL of chloroform, then wash it by shaking it for about 30 s with 5 mL of chloroform. Add 5 mL of concentrated hydrochloric acid to the combined extracts, then close the funnel and shake it for 3 min. Allow the layers to separate, then drain off and discard the chloroform layer.

Add 45 mL of water and 3 mL of 1% ammonium pyrrolidinedithiocarbamate-3% cupferron solution to the resulting solution and mix it thoroughly. Allow the solution to stand for about 5 min, then add 10 mL of chloroform, close the funnel and shake it for 1 min. Drain off and discard the chloroform phase. Extract the solution once more in a similar manner using 2 mL of ammonium pyrrolidinedithiocarbamate-cupferron solution and 5 mL of chloroform (Note 12), then wash the aqueous phase twice by shaking it for 1 min each time with 5 mL of chloroform. Transfer the aqueous phase to a 250-mL beaker and add 5 mL of 50% sulphuric acid. Heat the solution gently to remove the excess chloroform, then evaporate it to about 25 mL. Add 3 mL each of concentrated perchloric and nitric acids, cover the beaker and boil the solution to destroy organic material, then remove the cover and evaporate the solution until approximately 1.5 mL of sulphuric acid remains (Notes 9 and 13). Cool the solution, wash down the sides of the beaker with a small amount of water and evaporate the solution just to fumes of sulphur trioxide. Add 25 mL of water and heat the solution gently to dissolve the salts. Transfer the solution to a 100-mL volumetric flask and dilute it to volume with water.

Transfer suitable identical 4-20-mL aliquots of the resulting sample and blank solutions to 100-mL beakers. Add 2 mL of 5% ascorbic acid solution, 4 mL of 0.08% pyrocatechol violet solution and 1 mL of 50% ammonium acetate solution to

each solution, then proceed with the pH adjustment and the subsequent measurement of the absorbance of the aluminum-pyrocatechol violet complex as described above. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the reagent blank solution and determine the aluminum content of the aliquot by reference to the calibration curve.

B - Copper-base and nickel-copper alloys

(a) Aluminum content greater than 0.10%

Transfer 0.2-2 g of sample containing not more than 2 mg of aluminum to a 250-mL beaker (Note 14) and add 20 mL of 50% sulphuric acid and 5 mL of concentrated nitric acid. Cover the beaker and heat the mixture until the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool the solution, wash down the sides of the beaker with a small amount of water and evaporate the solution to fumes of sulphur trioxide again to ensure the complete removal of nitric acid. Add 50 mL of water and, if necessary, heat the solution gently to dissolve the salts. Cool the solution to room temperature, transfer it to a 200-mL volumetric flask and dilute it to volume with water. Transfer a 50-mL aliquot of the resulting solution to a mercury cathode cell, dilute it to 100 mL with water, then proceed with the mercury cathode separation, the acetylacetone and ammonium pyrrolidinedithiocarbamate-cupferron chloroform extractions and the subsequent determination of aluminum as described in Procedure A.

(b) Aluminum content 0.10% or less

Decompose 0.5-1 g of sample as described above using 7 mL of 50% sulphuric acid instead of 20 mL. Evaporate the solution to fumes of sulphur trioxide twice as described above, then add 50 mL of water and, if necessary, heat gently to dissolve the salts. Transfer the resulting solution to a mercury cathode cell, dilute it to 100 mL with water and proceed with the mercury cathode and other separation procedures and the ultimate determination of aluminum as described in Procedure A.

C - Molybdenum and tungsten metals

Transfer 0.5 g of powdered metal to a 30-mL platinum crucible and heat the crucible for 1 h at 600-640°C (Note 15). Cool the resulting oxide, then add 3 g of sodium carbonate and mix thoroughly. Cover the crucible and fuse the mixture by heating it for about 15 min at the full temperature of a blast burner. Cool the crucible, then transfer it and the cover to a covered 250-mL beaker containing 25 mL of water and 5 mL of 50% sulphuric acid. When the melt has dissolved, remove the crucible and the cover after washing them thoroughly with water and dilute the solution to approximately 50 mL with water (Note 10). In succession, add 5 mL of 30% hydrogen peroxide, 5 mL of 10% acetylacetone solution and 10 mL of 50% ammonium acetate solution, then proceed with the pH adjustment (Note 16), the acetylacetone and ammonium pyrrolidinedithiocarbamate-cupferron extractions and the subsequent determination of aluminum as described in Procedure A (Note 17).

NOTES

1. Because pyrocatechol violet - in powder form - changes or deteriorates on standing (1,2), the reagent should be tested before use and should satisfy the following criteria under the recommended conditions for complex formation:

   (a) Complex formation should be essentially instantaneous at room temperature.
   (b) The absorbance of the complex should remain constant for at least 2 h and should not decrease by more than 3% at the 40-µg level after 24 h.
   (c) The absorbance value obtained for 40 µg of aluminum should be approximately 1.05 at 578 nm - the wavelength of maximum absorption.
   (d) Beer's law should be obeyed for up to 40 µg of aluminum and the calibration curve should pass through the origin.

   A satisfactory solution of the reagent is stable for at least one month.

2. Approximately 3 mL of glacial acetic acid is

required for pH adjustment.

3. For steel and alloy samples of high chromium content - e.g., stainless steel and nickel-chromium alloys - decompose the sample as described in Procedure A (p 2) of the atomic-absorption method for aluminum and evaporate the solution to about 10 mL. Add about 50 mL of water and, if necessary, heat the solution gently to dissolve the salts. Using Whatman No. 541 paper, filter the solution into a 200-mL volumetric flask, wash the paper and the residue with water and 1% sulphuric acid as described in the above procedure and treat the paper and residue as described. After dissolving the sodium hydrogen sulphate melt in water (Note 6), add the resulting solution to the initial filtrate, dilute the solution to volume with water and proceed with the mercury cathode separation - using a 50-mL aliquot of the solution - as described in the subsequent part of this procedure. Add 3 mL of 50% sulphuric acid and 5 mL of concentrated hydrochloric acid to the solution obtained after the mercury cathode separation, evaporate the solution to 1.5-2 mL and proceed as described.
4. If the sample contains more than approximately 0.5% of silicon, evaporate the solution to fumes of sulphur trioxide to dehydrate the silica. Cool the solution to room temperature, add about 50 mL of water, heat the solution to dissolve the salts, then proceed as described.
5. Nitric acid is added to dissolve any elemental silicon present.
6. If the aluminum content of the acid-insoluble material is required, it can be determined separately in the resulting solution. In this case, add the volumes of hydrogen peroxide, acetylacetone and ammonium acetate solutions recommended in the subsequent part of the procedure and proceed with the pH adjustment, the extraction and the subsequent determination of aluminum as described. The total amount of aluminum present in the sample can then be determined by adding that found in the acid-soluble material to that found in the filtrate.
7. It may be necessary to filter the solution into the flask containing the initial filtrate to remove any yellow hydrated tungsten trioxide present.
8. The sample solution can be used for the determination of vanadium by the spectrophotometric-N-benzoyl-N-phenylhydroxylamine method (p 102) after evaporating a suitable aliquot of both the sample and reagent blank solutions to dryness to remove sulphuric acid. This should be followed by the dissolution of the residue in 8 mL of 12.5 M sulphuric acid and 5-10 mL of water, the addition of the recommended volumes of 25 M hydrofluoric acid and 10% ferrous ammonium sulphate and ammonium persulphate solutions and the extraction of the vanadium complex as described.
9. Sulphuric acid solutions of aluminum should not be evaporated to dryness. This results in the formation of an anhydrous aluminum sulphate that is virtually insoluble in water or in dilute acid. This causes a low result for aluminum (10).
10. Some flocculent silica - originally present as soluble silica in the initial sample filtrate - may be present at this stage but it does not interfere in the subsequent steps. If the subsequent extraction procedures cannot be completed the same day, allow the solution to stand overnight at this point.
11. Add 5 mL of 30% hydrogen peroxide if a 2-g sample of ferrovanadium was taken. Approximately 1 mL is required to complex 30 mg of vanadium. The solution containing vanadium should be yellow - not green - after the pH adjustment (9).
12. Five mL of 1% ammonium pyrrolidinedithiocarbamate-3% cupferron solution is sufficient for the removal of up to at least 5 mg of iron or copper. If the extract is still coloured at this stage, continue the extraction as described using 1-mL portions of the above solution and 5-mL portions of chloroform until a colourless extract is obtained.

13. If the solution is yellow or brown, repeat the nitric acid-perchloric acid treatment - adding more sulphuric acid if necessary - until the solution is colourless.
14. If the sample contains silicon, use a 250-mL teflon beaker and add 1 or 2 mL of concentrated hydrofluoric acid during the decomposition step.
15. Under these temperature conditions, the loss of molybdenum by volatilization as the trioxide does not exceed approximately 10 mg.
16. For tungsten solutions, adjust the pH to about 8 to dissolve insoluble tungsten compounds, then acidify the solution with 4 or 5 drops of 50% sulphuric acid and readjust the pH to 6.5 ± 0.1.
17. Aliquots greater than 20 mL are not recommended because of the high aluminum content - up to about 18 µg - of the reagent blank. This results largely from the sodium carbonate used in this procedure because lower blanks - 10 µg or less - are obtained in the methods involving acid decomposition procedures.

ACCURACY

Illustrated in Tables 1 and 2 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine aluminum in tin-, zinc- and cobalt-base alloys and in nickel oxide.

REFERENCES

1. Donaldson, E.M. "Determination of aluminum in molybdenum and tungsten metals, iron, steel and ferrous and non-ferrous alloys with pyrocatechol violet"; Talanta 18:905-915; 1971.

2. Idem, unpublished work.

3. Ryba, O., Cifka, J., Jezkova, D., Malat, M. and Suk, V. "Chemical indicators - IV: Complexes of pyrocatechol violet with tri- and quadrivalent metals"; Chem Listy 51:1462-1466; 1957; (Chem Abstr 51:16194c; 1957).

4. Suk, V. and Malat, M. "Pyrocatechol violet: Indicator for chelatometric titrations"; Chemist-Analyst 45:30-37; 1956.

5. Cifka, J., Ryba, O., Suk, V and Malat, M. "Chemical indicators - III: Complexes formed by pyrocatechol violet with bivalent metals"; Chem Listy 50:888-898; 1956; (Chem Abstr 50:11160e; 1956).

6. Budesinsky, B. "Complexes of metallochromic substances - V: Optimum conditions for metal complex formation and their relation to the complex composition"; Z Anal Chem 207:247-256; 1965.

7. Babko, A.K. and Shtokalo, M.I. "Reagents for the colorimetric determination of tantalum"; Ukr Khim Zh 29:963-967; 1963.

8. Golubtsova, R.B. and Yaroshenko, A.D. "Spectrophotometric determination of microgram amounts of chromium in anodic powders"; Zavod Lab 36:147-148; 1970.

9. Donaldson, E.M. "Determination of aluminum in iron, steel and ferrous and non-ferrous alloys by atomic-absorption spectrophotometry after a mercury cathode separation and extraction of the aluminum acetylacetone complex"; Talanta 28:461-467; 1981.

10. Kolthoff, I.M. and Elving, P.J. "Treatise on analytical chemistry" (Part II); New York, Interscience; 4:377; 1966.

ATOMIC-ABSORPTION DETERMINATION OF ANTIMONY IN COPPER METAL AND COPPER- AND LEAD-BASE ALLOYS AFTER SEPARATION BY IRON-LANTHANUM COLLECTION

PRINCIPLE

Antimony is separated from matrix elements by coprecipitating antimony (III) with hydrous ferric and lanthanum oxides from an ammoniacal, approximately pH 10, medium. The precipitate is dissolved in dilute hydrochloric acid and antimony is ultimately determined by atomic-absorption spectrophotometry at 217.6 nm in an oxidizing air-acetylene flame in a 15% hydrochloric acid-0.1% tartaric acid medium (1).

INTERFERENCES

Large amounts - e.g., 50 mg - of aluminum, zirconium and tin interfere in the coprecipitation of antimony (III) - at the 2-mg level - with 50 mg of lanthanum probably because they preferentially form similar compounds with lanthanum or partly soluble compounds with antimony. Up to approximately 25 mg of either aluminum, zirconium or tin or approximately 10 mg each of aluminum and tin, do not interfere in the coprecipitation of up to 2 mg of antimony. Up to 50 mg of either aluminum or tin do not interfere in the coprecipitation of up to 500 µg of antimony. Larger amounts can be tolerated if more lanthanum is used but this results in a bulkier precipitate that takes longer to filter. Furthermore, when the precipitate contains 50 mg or more of aluminum, the resultant solution passes very slowly through the filter paper. In the absence of aluminum, zirconium, tin and other hydrous oxides, 50 mg of lanthanum is sufficient for the coprecipitation of up to at least 10 mg of antimony (1).

Vanadium, in large amounts, causes a low result for antimony because vanadium (V) is reduced to the tetravalent state during the reduction of antimony with sodium metabisulphite. Probably the resultant vanadium (IV) is partly oxidized during the subsequent air-oxidation of iron (II) and causes some co-oxidation of antimony (III) to antimony (V). Chromium, in large amounts, also interferes because it forms an insoluble compound, which presumably retains some antimony, during the coprecipitation step. Milligram-quantities of vanadium and chromium do not cause significant error in the result. Up to at least 50 mg of manganese does not interfere in the coprecipitation step (1).

Possible interference from iron, lanthanum and hydrochloric acid is avoided by adding the same amounts that are present in the sample solution to the calibration solutions. Up to at least 500 µg/mL of copper, tin, aluminum, nickel, molybdenum, manganese or zinc, 1000 µg/mL of lead, 1500 µg/mL of iron or 200 µg/mL of arsenic can be present in the final solution without causing error in the antimony result. More than approximately 1000 µg/mL of lead produces a slightly high result and may result in the precipitation of lead chloride in the solution (1).

RANGE

This method is suitable for samples containing approximately 0.01 to 2% of antimony.

APPARATUS

GAS-DISPERSION TUBES. For maximum air-bubbling efficiency, these tubes should be bent at 90° so that the fritted glass tip is parallel to the bottom of a 400-mL beaker. For convenience, the air-inlet part of the tube can be bent at 90° in the opposite direction.

REAGENTS

STANDARD ANTIMONY SOLUTION, 100 µg/mL. Dissolve 0.2669 g of pure potassium antimony tartrate ($KSbO.C_4H_4O_6$) - dried at 105°C for 1 h - in water and dilute the solution to 1 L.

IRON (III) SULPHATE SOLUTION, 10 mg iron/mL. Dissolve 25 g of ferric sulphate monohydrate in about 400 mL of hot water containing 20 mL of 50% sul-

phuric acid, then cool the solution and dilute it to 500 mL with water.

LANTHANUM CHLORIDE SOLUTION, 10 mg lanthanum/mL. Dissolve 12.5 g of lanthanum chloride hexahydrate in water and dilute the solution to 500 mL.

AQUA REGIA. Mix 3 parts of concentrated hydrochloric acid with 1 part of concentrated nitric acid. Prepare the solution fresh as required.

TARTARIC ACID SOLUTION, 5% *m/v*.

AMMONIUM HYDROXIDE, 10% *V/V*.

HYDROCHLORIC ACID, 25 and 50% *V/V*.

SULPHURIC ACID, 50% *V/V*.

CALIBRATION SOLUTIONS

Add 2 mL of 5% tartaric acid solution, 15 mL of concentrated hydrochloric acid and 5 mL each of iron (III) sulphate and lanthanum chloride solutions to each of eight 100-mL volumetric flasks; then by burette, add to the first seven flasks 1, 3, 5, 7.5, 10, 15 and 20 mL, respectively, of the standard 100-µg/mL antimony solution. The contents of the last flask constitute the zero calibration solution. Dilute each solution to volume with water.

PROCEDURE

Transfer 0.1-0.5 g of sample (Notes 1-3) containing between 50 µg and about 2 mg of antimony to a 400-mL beaker. Add 25 mL of freshly prepared aqua regia (Note 4), cover the beaker and heat the mixture gently until all or most of the sample is decomposed. Add 25 mL of 50% sulphuric acid, heat the solution until the evolution of oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water and carefully evaporate the solution to dryness. Cool the beaker, then add 50 mL of 50% hydrochloric acid, cover the beaker and, if necessary, heat the solution gently to dissolve the salts - particularly lead sulphate. Cool the resulting solution to room temperature, add 3 g of sodium metabisulphite, mix the solution thoroughly and allow it to stand for about 5 min. Boil the covered solution for approximately 10 min to remove the excess sulphur dioxide, then add 25 mL of water. Place a gas-dispersion tube in the beaker and pass air through the solution at a fairly rapid rate for about 10 min to reoxidize any iron (II) present. Remove the tube after washing it thoroughly with water.

Add 5 mL each of iron (III) sulphate and lanthanum chloride solutions to the resulting solution, then add sufficient concentrated ammonium hydroxide to precipitate iron as the hydrous oxide. Add 75 mL in excess and heat the solution to the boiling point to coagulate the precipitate. Allow it to settle, then using Whatman No. 40 paper, filter the solution while it is hot. Wash the beaker twice and wash the paper and precipitate 3 times with 10% ammonium hydroxide. Discard the filtrate and washings and place a 100-mL volumetric flask containing 2 mL of 5% tartaric acid solution under the funnel. Wash down the sides of the beaker with 45 mL of 25% hydrochloric acid and add the resulting solution to the funnel containing the paper and precipitate. Wash the beaker twice with about 5-mL portions of water and add the washings to the funnel. Wash the paper 3 times with about 5-mL portions of 25% hydrochloric acid added from a plastic wash-bottle, then wash it twice with water. Discard the paper and dilute the solution to volume with water (Note 5).

Measure the absorbance of the resulting solution at 217.6 nm in an oxidizing air-acetylene flame (Note 6). Determine the antimony content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower antimony concentrations.

NOTES

1. A low result, caused by incomplete coprecipitation of antimony, will be obtained at the 2-mg level if more than about 25 mg of either aluminum or tin or more than about 10 mg of each is present. Up to 50 mg of either aluminum or tin will not interfere in the coprecipitation of up to 500 µg of antimony. Samples

containing more than about 100 mg of lead are not recommended because the lead chloride obtained after dissolving the hydrous oxide precipitate is not completely soluble in 15% hydrochloric acid.

2. If the expected antimony content is low, up to at least 1 g of sample can be taken for high-purity copper metal and for copper-base alloys of low aluminum and tin content (Note 1).
3. If the sample contains an appreciable amount of silicon, use a 400-mL teflon beaker and add 2 or 3 mL of concentrated hydrofluoric acid after the cover has been removed. Evaporate the solution to fumes of sulphur trioxide, then cool it to room temperature, add about 15 mL of water and heat the solution to dissolve the salts. Transfer the solution to a glass beaker, evaporate it to dryness and proceed as described. A low result will be obtained if the excess of sulphuric acid is not removed by evaporation.
4. The use of aqua regia during the sample decomposition step ensures that all the antimony will be present as antimony (V). This is important to avoid a low result if antimony is ultimately separated by xanthate extraction and determined spectrophotometrically by the iodide method as described on page 17.
5. Probably bismuth can also be determined in the resulting solution by atomic-absorption spectrophotometry (p 24) if the calibration solutions used for comparison purposes contain the same concentrations of iron, lanthanum and hydrochloric acid.
6. Approximately two- to five-fold scale expansion is recommended for the determination of about 3 µg/mL or less of antimony.

ACCURACY

Illustrated in Table 3 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine antimony in nickel-, zinc- and molybdenum-base alloys and metals.

REFERENCE

1. Donaldson, E.M. "Determination of antimony in concentrates, ores and non-ferrous materials by atomic-absorption spectrophotometry after iron-lanthanum collection, or by the iodide method after further xanthate extraction"; Talanta 26:999-1010; 1979.

SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY IN COPPER METAL AND COPPER- AND LEAD-BASE ALLOYS BY THE IODIDE METHOD AFTER SEPARATION BY IRON-LANTHANUM COLLECTION AND XANTHATE EXTRACTION

PRINCIPLE

Antimony is separated from matrix elements by coprecipitating antimony (III) with hydrous ferric and lanthanum oxides from an ammoniacal, approximately pH 10, medium. The precipitate is dissolved in 5 M hydrochloric acid-tartaric acid solution containing thiourea as a complexing agent for copper and stannous chloride as a reductant for iron (III). Tin is complexed with hydrofluoric acid and antimony is separated from iron, lanthanum and other elements by chloroform extraction of its ethyl xanthate complex. Antimony is ultimately determined spectrophotometrically by measuring the absorbance at either 331 or 425 nm of the yellow iodoantimonite ion formed in a 1.4 M sulphuric acid-0.42 M potassium iodide medium in a reducing - ascorbic acid - environment. The molar absorptivities of the complex at these wavelengths are 3.11×10^3 and 4.53×10^2 $L.mol^{-1}.mm^{-1}$, respectively (1).

INTERFERENCES

Nickel, which forms a coloured solution; bismuth, platinum, palladium and tin, which form soluble coloured compounds with iodide; lead, thallium, silver and copper, which form insoluble iodides; iron (III), which oxidizes iodide and liberates iodine; and molybdenum, vanadium and tungsten interfere in the determination of antimony as the iodide (2-4). Although platinum, palladium, thallium, molybdenum, vanadium and tungsten are not usually present in copper- and lead-base alloys they would ultimately be separated from antimony by the separation procedures described. Interference from bismuth and lead, and from iron (III), after it is reduced to iron (II) with stannous chloride, is avoided by separating antimony (III) from them by chloroform extraction of its ethyl xanthate complex from a 5 M hydrochloric acid medium. The coextraction of tin as the xanthate is prevented by complexing it with hydrofluoric acid. Interference from small amounts of coextracted bismuth is eliminated by washing the extract with a hydrochloric acid solution of the same acid concentration as the medium used for extraction. Up to approximately 10 mg of bismuth can be present in the sample without causing significant error in the result when the absorbance measurement is made at 331 nm (1).

Selenium (IV), tellurium (IV) and arsenic (III) are completely extracted into chloroform as xanthate complexes from 5 M hydrochloric acid. Copper (II) is partly extracted (5). However, selenium and tellurium do not interfere because they are reduced to the elemental state with stannous chloride before the extraction of antimony (III) xanthate. Interference from large amounts of nickel and copper is avoided by separating antimony from them and from various other elements - e.g., zinc, silver and cadmium - before the xanthate extraction step, by coprecipitating antimony (III) twice with hydrous ferric and lanthanum oxides from a strongly ammoniacal, approximately pH 10, medium. The coextraction of copper that is retained in the mixed hydrous oxide precipitate after a double coprecipitation step is largely prevented or inhibited by complexing it with thiourea before the extraction of antimony (III) xanthate. Up to at least 10 mg of arsenic, which is retained in the hydrous oxide precipitate and which is subsequently coextracted as the xanthate, does not interfere in the extraction of up to 2 mg of antimony or in the ultimate determination of small amounts at either 331 or 425 nm (1). More than the recommended amounts of all the elements - i.e., aluminum, zirconium, tin, vanadium and chromium - that interfere in the coprecipitation of antimony (III) with hydrous ferric and lanthanum oxides, as described in the atomic-

absorption method for antimony (p 12), also interfere in this method.

A low result will be obtained for antimony if the sample is decomposed with a mixture of nitric acid and either sulphuric or perchloric acid. This is because an unreactive antimony species - presumably in a mixed oxidation state - is formed under these conditions. Although this compound is completely coprecipitated with iron and lanthanum, it is not reduced with tin (II) when the precipitate is dissolved in 5 M hydrochloric acid containing stannous chloride and, consequently, it is not extracted as the xanthate. This error is prevented by oxidizing antimony completely to antimony (V) with aqua regia during the sample decomposition step. A low result will also be obtained if the xanthate extract is treated with the above acids and the solution is evaporated to fumes of sulphur trioxide before complex formation, or if the solution is evaporated to dryness in a teflon beaker and the salts are dissolved in dilute potassium hydroxide solution. In the first case, this is caused by the formation, in part, of basic antimony (V) compounds that are insoluble in dilute sulphuric acid. In the second case, it is caused by the formation of the unreactive antimony compound; this is insoluble in dilute potassium hydroxide solution and contaminates the teflon beaker. These errors are eliminated by treating the solution of the extract with aqua regia. This converts all the antimony to antimony (V) which is soluble in dilute potassium hydroxide solution (1).

RANGE

This method is suitable for samples containing approximately 0.0001 to 2% of antimony.

REAGENTS

STANDARD ANTIMONY SOLUTION, 0.1 mg/mL. Prepare the solution as described in the atomic-absorption method for antimony (p 12). Prepare 5- and 50-µg/mL solutions by diluting 5 and 50 mL, respectively, of the stock solution to 100 mL with water. Prepare the diluted solutions fresh as required.

POTASSIUM IODIDE-ASCORBIC ACID SOLUTION, 35% and 2.5% *m/V*, respectively. Prepare the solution fresh as required.

5 M HYDROCHLORIC ACID-STANNOUS CHLORIDE DIHYDRATE-TARTARIC ACID-THIOUREA SOLUTION, 43% *V/V*, 0.5% *m/V*, 2% *m/V* and 0.5% *m/V*, respectively. Prepare a sufficient volume of solution just before use.

5 M HYDROCHLORIC ACID-TARTARIC ACID SOLUTION. Dissolve 4 g of tartaric acid in water, add 430 mL of concentrated hydrochloric acid and dilute the solution to 1 L with water.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

THIOUREA SOLUTION, 5% *m/V*. Prepare the solution fresh as required.

AQUA REGIA. Mix 3 parts of concentrated hydrochloric acid with 1 part of concentrated nitric acid. Prepare the solution fresh as required.

POTASSIUM HYDROXIDE SOLUTION, 10% *m/V*. Store the solution in a plastic bottle.

TARTARIC ACID SOLUTION, 5% *m/V*.

AMMONIUM HYDROXIDE, 10% *V/V*.

SULPHURIC ACID, 50% *V/V*.

HYDROCHLORIC ACID, 25% *V/V*.

NITRIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION CURVES

Add 4 mL of 50% sulphuric acid and 1 mL of 5% tartaric acid solution to each of fifteen 25-mL volumetric flasks; then by burette, add to the first five flasks 1, 2, 3, 4 and 5 mL, respectively, of the dilute standard 5- µg/mL antimony solution. Add to the next nine flasks 1, 1.5, 2,

3, 4, 6, 8, 10 and 12 mL, respectively, of the dilute standard 50-µg/mL antimony solution. The contents of the last flask constitute the blank. If necessary, dilute each solution to approximately 15 mL with water and cool it to room temperature in a water-bath. Add 5 mL of freshly prepared 35% potassium iodide-2.5% ascorbic acid solution to each flask and dilute the solutions to volume with water. Allow the solutions to stand for about 30 min to complete the complex formation, then measure the absorbance of the blank solution and of each of the five solutions in the first series at 331 nm against water as the reference solution, using 40-mm cells. Measure the absorbance of the blank solution, of the solution of highest antimony content in the first series, and of each of the four solutions of lowest antimony content in the second series in a similar manner at 425 nm using 40-mm cells. Measure the absorbance of the blank solution and of each of the seven solutions of highest antimony content in the second series at 425 nm using 10-mm cells. Correct the absorbance value obtained for each antimony-iodide solution by subtracting the corresponding blank value. Plot micrograms of antimony vs absorbance for each series of measurements.

PROCEDURE

In this procedure a reagent blank, to which approximately 50 mg each of lanthanum and iron (III) are ultimately added, is carried along with the samples.

Following sample decomposition and the coprecipitation of antimony with hydrous ferric and lanthanum oxides (Note 1) as described in the atomic-absorption method for antimony (p 13), filter the hot solution using a short-stemmed funnel and Whatman No. 40 paper. Unless more than approximately 75 mg of copper or nickel is present, wash the beaker twice and wash the paper and precipitate 3 times with 10% ammonium hydroxide (Note 2). Discard the filtrate and washings.

If more than approximately 75 mg of copper or nickel is present, wash the beaker and the precipitate each once with 10% ammonium hydroxide. Place the original beaker under the funnel and add 25 mL of 25% hydrochloric acid to the funnel to dissolve the precipitate. Wash the paper 3 times with 25% hydrochloric acid added from a plastic wash-bottle, then wash down the sides of the beaker with the same acid solution. Reprecipitate the iron and lanthanum and filter and wash the precipitate as described above (Note 2). Discard the filtrate.

Transfer the funnel containing the precipitate to a 250-mL separatory funnel marked at 100 mL and wash down the sides of the beaker, in which the precipitation was carried out, with 25 mL of freshly prepared 5 M hydrochloric acid-stannous chloride-tartaric acid-thiourea solution (Note 3). Add the resulting solution to the funnel containing the precipitate and wash the beaker 3 times with the same 5 M acid solution added from a plastic wash-bottle. Wash the paper 3 times with the same acid solution, then discard it. Dilute the solution to the 100-mL mark with the same 5 M acid solution (Note 4), then add 2 mL of concentrated hydrofluoric acid and mix the solution thoroughly (Note 5).

Add 10 mL of chloroform to the resulting solution, then add 1 mL of freshly prepared 20% potassium ethyl xanthate solution (Note 6). Close the funnel and shake it for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-mL separatory funnel. Extract the aqueous phase two more times in a similar manner with 10- and 5-mL portions of chloroform and 1 and 0.5 mL of xanthate solution, respectively, then wash the aqueous phase by shaking it for about 30 s with 3 mL of chloroform. Add 30 mL of 5 M hydrochloric acid-tartaric acid solution and 1 mL of 5% thiourea solution (Note 3) to the combined extracts, then close the funnel and shake it for 1 min. After the layers have separated, drain the chloroform phase into a 100-mL teflon beaker (Note 7). Add 5 mL of chloroform and 0.5 mL of xanthate solution to the aqueous phase and shake the funnel for 1 min. Allow the layers to separate and drain the chloroform phase into the beaker containing the initial extract, then wash the aqueous phase by shaking it for about 30 s with 5 mL of chloroform.

Add 8 mL of 50% nitric acid to the resulting extract and heat the mixture in a hot water-bath to remove the chloroform. Add 1 mL of concentrated perchloric acid and 0.5 mL of 50% sulphuric acid, then cover the beaker and heat the solution until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to fumes of perchloric acid. Cool the solution to room temperature, then add 5 drops of freshly prepared aqua regia and mix the solution thoroughly. Wash down the sides of the beaker with water and evaporate the solution until the diameter of the drop remaining in the bottom of the beaker is 3 or 4 mm. Cool the beaker in a water-bath, then wash down the sides with 5 mL of 10% potassium hydroxide solution added from a pipette and heat the solution gently for about 5 min. Cool the solution slightly, then add 1 mL of 5% tartaric acid solution and 4.5 mL (Note 8) of 50% sulphuric acid. Heat the solution gently again for about 5 min, then add approximately 5 mL of water and cool the solution to room temperature in a water-bath (Note 9).

If the sample contains 600 µg or less of antimony, transfer the sample and blank solutions to 25-mL volumetric flasks containing 5 mL of 35% potassium iodide-2.5% ascorbic acid solution (Note 10). Dilute the solutions to volume with water and, after 30 min, proceed with the subsequent measurement of the absorbance as described above (Note 11), using either 10- or 40-mm cells and a wavelength of 425 or 331 nm as required. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the reagent blank solution and determine the antimony content of the sample solution by reference to the appropriate calibration curve.

If the sample contains more than 600 µg of antimony, transfer the sample and blank solutions to volumetric flasks of appropriate size - 25 or 50 mL. Add sufficient additional 5% tartaric acid solution so that 1 mL will be present for each 10 mL of final solution and dilute the solutions to volume with water. Transfer a 10-mL aliquot of each solution to a 25-mL volumetric flask and add sufficient 50% sulphuric acid so that 4 mL will be present. Cool the resulting solutions to room temperature, then proceed with the addition of potassium iodide-ascorbic acid solution and the subsequent determination of the antimony content of the aliquot as described above, using 10- or 40-mm cells as required and a wavelength of 425 nm.

NOTES

1. The sample can contain up to at least 350 mg of lead. This method is also applicable to molybdenum alloys. However, a double coprecipitation of antimony is required to separate it from most of the molybdenum. Interference from residual molybdenum, which is partly coextracted as the reddish purple xanthate complex, and which causes a high result for small amounts of antimony when absorbance measurements are made at 331 nm, can be avoided by measuring the absorbance of the iodide complex at 425 nm. Molybdenum also inhibits complex formation slightly when about 100 µg or more of antimony is present, but this effect can be eliminated or minimized by allowing the solution to stand for about 24 h before measuring the absorbance.
2. If the subsequent xanthate extraction cannot be completed the same day, allow the precipitate to stand overnight at this point.
3. Thiourea can be omitted if it is known that the sample contains little or no copper.
4. The solution should be colourless at this point. Sufficient stannous chloride is present to reduce up to approximately 240 mg of iron (III).
5. To minimize the attack of hydrofluoric acid on glass, the subsequent extraction of antimony (III) xanthate should proceed immediately after the hydrofluoric acid has been added. Similarly, the funnel should be washed immediately after the extraction has been completed.
6. The xanthate solution should be added by pipette using a suction bulb or by using a graduated or marked medicine dropper and the

extraction should be carried out in a fume hood. Prolonged exposure to xanthate vapour can produce an allergic reaction.

7. Glass beakers should not be employed because the potassium hydroxide solution that is used in the subsequent part of the procedure may leach antimony or lead from the glass. Teflon beakers may become partly discoloured - i.e., yellowish brown or black - inside because of the subsequent use of aqua regia to oxidize antimony to antimony (V). Before the beakers are used again, this discolouration should be removed by heating perchloric acid to dense fumes in the covered beaker.
8. The additional 0.5 mL of 50% sulphuric acid that is added to the sample solution - as compared with the calibration solutions - is required to react with the potassium hydroxide.
9. Salts may crystallize from the solution on standing but they will redissolve when the solution is ultimately diluted and mixed thoroughly.
10. The presence of arsenic is signified by a deep yellow or orange colour caused by iodine that is liberated during the reduction of arsenic (V) by potassium iodide. The iodine is subsequently reduced by ascorbic acid when the solution is mixed.
11. If the solution is slightly opalescent, filter it through a dry Whatman No. 42 filter paper before the spectrophotometric measurement.

ACCURACY

Illustrated in Table 3 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine antimony in nickel- and zinc-base alloys and metals.

REFERENCES

1. Donaldson, E.M. "Determination of antimony in concentrates, ores and non-ferrous materials by atomic-absorption spectrophotometry after iron-lanthanum collection, or by the iodide method after further xanthate extraction"; Talanta 26:999-1010; 1979.

2. Elkind, A., Goyer, K.H. and Boltz, D.F. "Ultraviolet spectrophotometric determination of antimony as iodoantimonous acid"; Anal Chem 25:1744-1745; 1953.

3. McChesney, E.W. "Colorimetric micromethod for determination of antimony in biological materials with concomitant determination of bismuth"; ibid 18:146-149; 1946.

4. Lisicki, N.M. and Boltz, D.F. "Ultraviolet spectrophotometric determination of bismuth by iodide and thiourea methods"; ibid 27:1722-1724; 1955.

5. Donaldson, E.M. "Chloroform extraction of metal ethyl xanthates from hydrochloric acid media"; Talanta 23:411-416; 1976.

SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC IN COPPER METAL AND COPPER-BASE ALLOYS BY THE MOLYBDENUM BLUE METHOD AFTER SEPARATION BY IRON COLLECTION AND XANTHATE EXTRACTION

PRINCIPLE

Arsenic is separated from matrix elements by coprecipitating arsenic (V) with hydrous ferric oxide from an ammoniacal medium. The precipitate is dissolved in approximately 2 M hydrochloric acid and arsenic is ultimately reduced to arsenic (III) with iron (II) in an 11 M hydrochloric acid medium and separated from iron and other coprecipitated elements by chloroform extraction of its ethyl xanthate complex. Arsenic in the extract is oxidized to arsenic (V) with bromine in carbon tetrachloride and is back-extracted into water (1). Arsenic is ultimately determined spectrophotometrically by measuring the absorbance at 845 nm of the blue reduced heteropoly arsenomolybdic acid complex formed in a 0.23 M sulphuric acid-0.001 M ammonium molybdate medium in the presence of hydrazine sulphate as reductant (2). The molar absorptivity of the complex at this wavelength is 2.55×10^3 $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCES

Numerous elements form ethyl xanthate complexes that can be extracted into chloroform from dilute hydrochloric acid media, but only platinum (IV), palladium (II), gold (III), selenium (IV) and tellurium (IV) - also selenium (VI) and tellurium (VI) after reduction by chloride ion - are extracted, either completely or to a large extent, from about 10-12 M hydrochloric acid media (3). Iron (III), copper (II) and molybdenum (VI) are slightly extracted from concentrated - i.e., 12 M - hydrochloric acid, and germanium and antimony (V) are partly extracted as their chlorocomplexes (3,4). Although platinum, palladium, gold and molybdenum are not usually present in copper-base alloys, they would ultimately be separated from arsenic by the coprecipitation step. Up to at least 3 mg each of iron (III) and copper (II), 400 µg of selenium (IV) and 500 µg of tellurium (IV) do not interfere during complex formation. Selenium and tellurium are reduced to the elemental state by iron (II) during the reduction of arsenic (1).

Germanium, phosphorus and silicon, which form similar reduced heteropoly molybdic acid complexes under the conditions employed for the formation of the arsenic complex (5), do not interfere. Phosphorus and silicon are not extracted as xanthate complexes, and interference from germanium is avoided by volatilizing it as the tetrachloride during the sample decomposition step. Tin (IV), antimony (V), bismuth and lead are coprecipitated with arsenic and iron from an ammoniacal medium. A large amount of lead and up to 50 mg of bismuth and antimony do not interfere. However, any tin present as insoluble metastannic acid before the separation of arsenic by coprecipitation with hydrous ferric oxide causes a low result for arsenic because of the formation of an insoluble tin-arsenic compound. This interference is eliminated during the sample decomposition step by dissolving metastannic acid with concentrated hydrochloric acid and then evaporating the solution to fumes of sulphur trioxide (1).

Large amounts of sulphate salts that are retained in the hydrous oxide precipitate after a single coprecipitation step may interfere if they are not completely dissolved in the 11 M hydrochloric acid medium used for the extraction of arsenic xanthate (1).

RANGE

This method is suitable for samples containing approximately 0.0001 to 1% of arsenic but material containing higher concentrations can also be analyzed with reasonable accuracy.

REAGENTS

STANDARD ARSENIC SOLUTION, 0.1 mg/mL. Dissolve 0.1320 g of pure arsenic trioxide (As_2O_3) in 10 mL of warm 2% sodium hydroxide solution. Dilute the solution to about 50 mL with water and add 2 drops of 0.2% phenolphthalein indicator solution. Add 10% sulphuric acid, by drops, until the solution is colourless, then dilute it to 1 L with water and transfer it to a plastic bottle. Prepare a 10-µg/mL solution by diluting 10 mL of this stock solution to 100 mL with water. Prepare the diluted solution fresh as required.

AMMONIUM MOLYBDATE SOLUTION, 1% *m/V* in 2.3 M sulphuric acid. Add 128 mL of concentrated sulphuric acid to about 800 mL of water and cool the solution to room temperature. Dissolve 10 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in about 50 mL of warm water and cool the solution to room temperature. Transfer both solutions to a 1-L volumetric flask and dilute the resulting solution to volume with water. Store the solution in a plastic bottle.

HYDRAZINE SULPHATE SOLUTION, 0.5% *m/V*. Prepare a fresh solution every five days.

IRON (III) SULPHATE SOLUTION, 20 mg iron/mL. Dissolve 25 g of ferric sulphate monohydrate in about 200 mL of hot water containing 10 mL of 50% sulphuric acid, then cool the solution and dilute it to 250 mL with water.

IRON (II) SULPHATE SOLUTION, 5% *m/V*. Dissolve 5 g of the reagent in 100 mL of hot concentrated hydrochloric acid and cool the solution to room temperature. Prepare the solution fresh as required.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

Phenolphthalein indicator solution, 0.2% *m/V* in ethyl alcohol. Store the solution in a dropping bottle.

BROMINE SOLUTION, 20% *V/V* in carbon tetrachloride.

BROMINE WATER.

SULPHURIC ACID, 50% *V/V*.

HYDROCHLORIC ACID, 15% *V/V*.

AMMONIUM HYDROXIDE, 5% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION CURVES

Add 15 mL of bromine water to each of eight 150-mL beakers (Note 1); then by burette, add to the last seven beakers 0.5, 1, 2.5, 5, 7.5, 10 and 15 mL, respectively, of the dilute standard 10-µg/mL arsenic solution. The contents of the first beaker constitute the blank. Heat each solution until it is free of bromine and, if necessary, evaporate it to approximately 20 mL. Transfer the solutions to 50-mL volumetric flasks and dilute them to about 40 mL with water. Add 5 mL of 1% ammonium molybdate solution and 1 mL of 0.5% hydrazine sulphate solution to each flask, dilute the solutions to approximately 48 mL with water, then close the flasks and mix the solutions thoroughly. Loosen the stoppers and place the flasks in a boiling water-bath for 30 min, then remove the flasks, cool the solutions to room temperature in a water-bath and dilute them to volume with water (Note 2). Measure the absorbance of the blank solution and of each of the three solutions of lowest arsenic content at 845 nm against water as the reference solution, using 40-mm cells. Measure the absorbance of the blank solution and of each of the five solutions of lowest arsenic content in a similar manner, using 20-mm cells, then measure the absorbance of the blank and of the six solutions of highest arsenic content using 10-mm cells. Correct the absorbance value obtained for each arsenic-molybdenum blue solution by subtracting the corresponding blank value. Plot micrograms of arsenic vs absorbance for each series of measurements.

PROCEDURE

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

Transfer 0.2-1 g of sample containing up to about 2 mg of arsenic to a 250-mL beaker. Cover the beaker and add 15 mL each of water and concentrated nitric acid, 10 mL of concentrated hydrochloric acid and 25 mL of 50% sulphuric acid. Heat the mixture until the evolution of oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water and carefully evaporate the solution to fumes of sulphur trioxide. Cool the solution, add about 100 mL of water, 5 mL of concentrated hydrochloric acid and 4 mL of iron (III) sulphate solution. Cover the beaker and heat the solution to dissolve the soluble salts.

Add sufficient concentrated ammonium hydroxide to precipitate iron as the hydrous oxide, then add 5 mL in excess and boil the solution to coagulate the precipitate. Allow it to settle, then using Whatman No. 40 paper, filter the hot solution and transfer the bulk of any insoluble material and lead sulphate to the filter paper with a jet of 5% ammonium hydroxide. Wash the paper and the precipitate twice with 5% ammonium hydroxide and discard the filtrate. Place the original beaker under the funnel and dissolve the precipitate with hot 15% hydrochloric acid added from a wash-bottle. Wash the paper 3 times with the same hot acid solution, then discard it. Wash down the sides of the beaker with the hot acid solution, then reprecipitate the iron and filter the precipitate as described above. Wash the beaker twice and wash the paper and precipitate 3 times with 5% ammonium hydroxide, then dissolve the precipitate with hot 15% hydrochloric acid again and collect the resulting solution in the original beaker. Wash the paper 3 times with the hot acid solution (Note 3), then discard it. Wash down the sides of the beaker with the hot acid solution and evaporate the solution to approximately 25 mL on a hot-plate (Note 4), then evaporate it to about 3 mL in a hot water-bath. Cool the solution to room temperature and add 20 mL of concentrated hydrochloric acid and 3 mL of water. Using a rubber-tipped stirring rod, detach any salts adhering to the bottom of the beaker, then wash the rod with concentrated hydrochloric acid added from a plastic wash-bottle.

Allow the resulting solution to stand at room temperature (Note 5) until the salts have dissolved (Note 6), then add 10 mL of freshly prepared 5% iron (II) sulphate solution and mix the solution thoroughly. Transfer the solution to a 125-mL separatory funnel marked at 50 mL, using concentrated hydrochloric acid to wash the beaker and, if necessary, dilute the solution to the mark with concentrated hydrochloric acid. Add 10 mL of chloroform to the funnel, then add 1 mL of freshly prepared 20% potassium ethyl xanthate solution, close the funnel and extract immediately (Note 7) by shaking it for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-mL separatory funnel. Extract the aqueous phase two more times in a similar manner with 10- and 5-mL portions of chloroform and 1 and 0.5 mL of xanthate solution, respectively, then wash the aqueous phase by shaking it for about 30 s with 5 mL of chloroform. Add 5 mL of 20% bromine-carbon tetrachloride solution to the combined extracts, close the funnel and mix the solution thoroughly. Allow the solution to stand for about 5 min to ensure the complete oxidation of arsenic (III) to arsenic (V), then add 15 mL of water, close the funnel and shake it for 1 min (Note 8). Allow several minutes for the layers to separate, then drain off and discard the chloroform-carbon tetrachloride phase. Drain the aqueous phase into a 150-mL beaker and wash the funnel 3 times with small portions of water. Add the washings to the aqueous phase. Heat the resulting solution gently to remove bromine and the excess of chloroform, then evaporate it to approximately 20 mL and cool it to room temperature.

If the sample contains 150 µg or less of arsenic, transfer the sample and blank solutions to 50-mL volumetric flasks, dilute them to abut 40 mL with water and proceed with the formation of the blue reduced arsenomolybdic acid complex and the subsequent measurement of the absorbance as described above, using 10-, 20- or 40-mm cells as required. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the reagent blank solution and determine the arsenic content of the sample solu-

tion by reference to the appropriate calibration curve.

If the sample contains more than 150 µg of arsenic, transfer the sample and blank solutions to volumetric flasks of appropriate size - 50-200 mL - and dilute them to volume with water. Transfer a suitable identical aliquot - up to 40 mL - of each solution to 50-mL volumetric flasks and proceed with the complex formation and subsequent determination of the arsenic content of the aliquot as described above.

NOTES

1. Glassware should be 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.
2. The blue reduced arsenomolybdic acid complex that is formed under these conditions is stable for at least 24 h.
3. Any lead chloride present at this stage will redissolve during the subsequent evaporation of the solution.
4. A low result will be obtained for arsenic if the solution is allowed to evaporate to dryness on a hot-plate.
5. Because arsenic (V) is reduced by chloride ion in relatively concentrated hydrochloric acid media, arsenic (III) will be lost by volatilization if the solution is heated to dissolve the salts.
6. If only a small amount of salts are present, add the recommended volume of iron (II) sulphate solution and transfer the solution and the salts to the separatory funnel as described. The salts will dissolve during the subsequent extraction step. If a large amount is present, it may be necessary to allow the solution to stand overnight.
7. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.
8. A low result will be obtained for arsenic if the aqueous phase containing arsenic (V) is allowed to remain in contact with the chloroform phase overnight.

ACCURACY

Illustrated in Table 4 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine arsenic in nickel-, zinc-, lead- and molybdenum-base alloys and metals.

REFERENCES

1. Donaldson, E.M. "Spectrophotometric determination of arsenic in concentrates and copper-base alloys by the molybdenum blue method after separation by iron collection and xanthate extraction"; Talanta 24:105-110; 1977.

2. American Society for Testing and Materials. "Emission spectroscopy - chemical analysis of metals; sampling and analysis of metal bearing ores"; Am Soc Test Mater Book ASTM Stand Part 32:E360-70T:990-991; 1973.

3. Donaldson, E.M. "Chloroform extraction of metal ethyl xanthates from hydrochloric acid media"; Talanta 23:411-416; 1976.

4. Idem. "Spectrophotometric determination of tellurium in concentrates and brasses by chloroform extraction of the tellurium (IV) hexabromide-diantipyrylmethane complex after separations by iron collection and xanthate extraction"; ibid 23:823-827; 1976.

5. Sandell, E.B. "Colorimetric determination of traces of metals" (3rd ed); New York, Interscience; 278-282; 1959.

ATOMIC-ABSORPTION DETERMINATION OF BISMUTH IN COPPER METAL AND COPPER-BASE ALLOYS AFTER SEPARATION BY IRON COLLECTION

PRINCIPLE

Bismuth is separated from matrix elements by coprecipitating it with hydrous ferric oxide from an ammoniacal medium. The precipitate is dissolved in dilute hydrochloric acid and bismuth is ultimately determined by atomic-absorption spectrophotometry at 223.1 nm in an oxidizing air-acetylene flame in a 20% hydrochloric acid medium (1).

INTERFERENCES

The coprecipitation procedure separates bismuth from large amounts of copper, zinc, nickel, cobalt and cadmium. Up to 50 mg - or 500 µg/mL in the final solution - of manganese (II), antimony (V), aluminum or tin (IV), which also form hydrous oxides, do not interfere in the coprecipitation or in the subsequent determination of bismuth. Larger amounts of tin and antimony cause low results for bismuth because of the slow and incomplete dissolution of the precipitate. A large amount of aluminum results in a solution that passes very slowly through the filter paper. More than 500 µg/mL of aluminum also produces a slightly high result for bismuth (1).

Lead is retained in the precipitate as lead sulphate and lead chloride which are subsequently dissolved when the precipitate is dissolved with hydrochloric acid. Up to 2000 µg/mL of lead in the final solution does not interfere but a larger amount may result in the precipitation of lead chloride. Up to at least 500 µg/mL of nickel, copper (II) or zinc, 300 µg/mL of arsenic (V) or 50 µg/mL of indium can be present in the final solution without interfering in the determination of bismuth. Possible interference from iron and from hydrochloric acid is avoided by adding the same amounts that are present in the sample solution to the calibration solutions (1).

Note: For samples containing large amounts of lead, aluminum, antimony or tin, the atomic-absorption-diethyldithiocarbamate extraction method for bismuth (p 26) is recommended.

RANGE

This method is suitable for samples containing approximately 0.001 to 0.5% of bismuth but material containing higher concentrations can also be analyzed with reasonable accuracy.

REAGENTS

STANDARD BISMUTH SOLUTION, 1000 µg/mL. Dissolve 0.5000 g of pure bismuth metal in 20 mL of concentrated nitric acid, cool the solution and dilute it to 500 mL with water. Prepare a 100-µg/mL solution by diluting 25 mL of this stock solution to 250 mL with water. Prepare the diluted solution fresh as required.

IRON (III) SULPHATE SOLUTION, 10 mg iron/mL. Dissolve 25 g of ferric sulphate monohydrate in about 400 mL of hot water containing 5 mL of concentrated sulphuric acid, then cool the solution and dilute it to 500 mL with water.

HYDROCHLORIC ACID, 20% *V/V*.

AMMONIUM HYDROXIDE, 10% *V/V*.

CALIBRATION SOLUTIONS

Add 20 mL of concentrated hydrochloric acid and 10 mL of iron (III) sulphate solution to eight 100-mL volumetric flasks, then by burette, add to the first seven flasks 0.5, 1, 2, 3, 5, 7.5 and 10 mL, respectively, of the dilute standard 100-µg/mL bismuth solution. The contents of the last flask constitute the zero calibration solu-

tion. Dilute each solution to volume with water (Note 1).

PROCEDURE

Transfer 0.2-0.5 g of sample (Notes 2-4) containing up to about 1 mg of bismuth to a 400-mL beaker, then cover the beaker and add 10 mL each of water and concentrated nitric acid and 20 mL of 50% sulphuric acid. When the sample has dissolved, heat the solution until the evolution of oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution and add about 100 mL of water, 5 mL of concentrated hydrochloric acid and 10 mL of iron (III) sulphate solution. Cover the beaker and heat the solution to dissolve the soluble salts.

Add sufficient concentrated ammonium hydroxide to precipitate iron as the hydrous oxide, then add 5 mL in excess and boil the solution to coagulate the precipitate. Allow it to settle, then using Whatman No. 40 paper, filter the hot solution and wash the beaker twice and wash the paper and precipitate 3 times with 10% ammonium hydroxide. Discard the filtrate and washings and place a 100-mL volumetric flask under the funnel. Wash down the sides of the beaker with 30 mL of 20% hydrochloric acid and add the resulting solution to the funnel containing the paper and precipitate. Wash the beaker twice with 20% hydrochloric acid added from a plastic wash-bottle and add the washings to the funnel. Wash the paper 3 times with the same acid solution. Discard the paper and dilute the solution to volume with 20% hydrochloric acid.

Measure the absorbance of the resulting solution at 223.1 nm in an oxidizing air-acetylene flame (Note 5). Determine the bismuth content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower bismuth concentrations.

NOTES

1. The calibration solutions should be prepared fresh every week because they are not stable on prolonged standing.
2. This method is not recommended for samples containing more than 50 mg of aluminum, antimony or tin or more than 200 mg of lead.
3. Samples containing more than 1 mg of bismuth can be taken if the final solution is diluted to an appropriate volume with 20% hydrochloric acid and if the calibration solutions contain approximately the same concentration of iron (III).
4. Up to 1 g of sample can be taken unless large amounts of other elements that form insoluble hydrous oxides (Note 2) are present.
5. Approximately two- to five-fold scale expansion is recommended for the determination of about 2 µg/mL or less of bismuth.

ACCURACY

Illustrated in Table 5 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine bismuth in nickel-, zinc- and molybdenum-base alloys and metals.

REFERENCE

1. Donaldson, E.M. "Determination of bismuth in ores, concentrates and non-ferrous alloys by atomic-absorption spectrophotometry after separation by diethyldithiocarbamate extraction or iron collection"; Talanta 26:1119-1123; 1979.

ATOMIC-ABSORPTION DETERMINATION OF BISMUTH IN COPPER METAL AND COPPER-, TIN- AND LEAD-BASE ALLOYS AFTER SEPARATION BY DIETHYLDITHIOCARBAMATE EXTRACTION

PRINCIPLE

Bismuth is separated from matrix elements by extraction of its diethyldithiocarbamate complex at pH 11.5-12.0 from a sodium hydroxide medium containing citric acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA) and potassium cyanide as complexing agents (1,2). Bismuth is ultimately determined by atomic-absorption spectrophotometry at 223.1 nm in an oxidizing air-acetylene flame in a 20% hydrochloric acid medium (1).

INTERFERENCES

In the presence of approximately 6 g of EDTA and 7 g of potassium cyanide, up to 500 mg of copper (II), molybdenum (VI), zinc and nickel, up to 250 mg of iron (III), up to 200 mg of tin (IV), up to 100 mg of cadmium, antimony (V), manganese (II), aluminum and zirconium, and up to 50 mg of arsenic (V) and phosphorus (V) do not interfere in the extraction of bismuth as the diethyldithiocarbamate complex. The extraction procedure separates bismuth from all elements except lead and thallium (III) (2). Up to approximately 17 mg of lead is coextracted at the 300-mg level, but up to about 2000 µg/mL does not interfere in the subsequent determination of bismuth. Coextracted thallium also does not interfere. Possible interference from hydrochloric acid is avoided by adding the same amount that is present in the sample solution to the calibration solutions (1).

RANGE

This method is suitable for samples containing approximately 0.002 to 0.5% of bismuth but material containing higher concentrations can also be analyzed with reasonable accuracy.

REAGENTS

STANDARD BISMUTH SOLUTION, 100 µg/mL. Prepare the solution as described in the atomic-absorption-iron collection method for bismuth (p 24).

CITRIC ACID-TARTARIC ACID SOLUTION, 25% each, *m/V*.

EDTA, disodium salt-sodium hydroxide solution, 12% each, *m/V*. Store the solution in a plastic bottle.

SODIUM HYDROXIDE SOLUTION, 50% *m/V*. Store the solution in a plastic bottle.

POTASSIUM CYANIDE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

SODIUM DIETHYLDITHIOCARBAMATE SOLUTION, 1% *m/V*. Prepare the solution fresh as required.

NITRIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION SOLUTIONS

Add 20 mL of concentrated hydrochloric acid to eight 100-mL volumetric flasks, then by burette, add to the first seven flasks 0.5, 1, 2, 3, 5, 7.5 and 10 mL, respectively, of the standard 100-µg/mL bismuth solution. The contents of the last flask constitute the zero calibration solution. Dilute each solution to volume with water (Note 1).

PROCEDURE

Following the decomposition of 0.2-0.5 g of sample (Note 2) containing up to about 1 mg of bismuth (Note 3) as described in the atomic-absorption-iron collection method for bismuth (p 25), evaporate the solution until copious fumes of sulphur trioxide are evolved (Note 4). Cool the solution to room temperature, add about 40 mL of water, then if lead sulphate is present, add 5

or 10 g of sodium chloride (Note 5). If necessary, heat the solution gently to dissolve the sodium salts and lead sulphate, then add 20 mL of 25% citric acid-25% tartaric acid solution, mix the solution (Note 6) and add 50 mL of 12% EDTA-12% sodium hydroxide solution. With the aid of a pH meter, if necessary (Note 7), or a small piece of red litmus paper added to the solution, make the solution alkaline - pH 7-11 - by adding 50% sodium hydroxide solution. Cool the resulting solution to room temperature in a water-bath, then adjust the pH to 11.75 ± 0.25 with 50% sodium hydroxide solution.

Transfer the resulting solution to a 250-mL separatory funnel, add 30 mL of freshly prepared 20% potassium cyanide solution and mix the solution thoroughly. Add 5 mL of freshly prepared 1% sodium diethyldithiocarbamate solution, then add 10 mL of chloroform (Note 8), close the funnel and shake it for 1 min. Allow several minutes for the layers to separate, then drain the chloroform extract into a 150-mL beaker. Extract the aqueous phase two more times in a similar manner with 10- and 5-mL portions of chloroform, then wash it by shaking it for about 30 s with 5 mL of chloroform. Add 10 mL of 50% nitric acid to the combined extracts, heat the mixture in a hot water-bath to remove the chloroform, then cover the beaker and add 10 mL of concentrated perchloric acid. Evaporate the solution to fumes of perchloric acid and continue to fume it for approximately 15 min to ensure the complete destruction of organic material. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to dryness. Add sufficient concentrated hydrochloric acid so that the concentration in the final solution will be approximately 20% by volume and warm the solution gently to dissolve the salts. Transfer the solution to a volumetric flask of appropriate size - 10-100 mL - and dilute it to volume with water.

Measure the absorbance of the resulting solution at 223.1 nm in an oxidizing air-acetylene flame (Note 9). Determine the bismuth content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower bismuth concentrations.

NOTES

1. The calibration solutions should be prepared fresh every week because they are not stable on prolonged standing.
2. A larger sample should not be used unless the volume of EDTA-sodium hydroxide solution that is subsequently used for masking purposes is increased correspondingly.
3. Samples containing more than 0.5% of bismuth can be analyzed if a small sample - 0.05-0.1 g - is taken, or if a suitable aliquot is taken of the solution obtained after the addition of sodium chloride - if necessary - and dissolution of the salts by heating.
4. A low result will be obtained if the solution is evaporated to dryness. If this occurs, add 20 mL each of 50% sulphuric acid and water, heat the mixture to dissolve the salts, then evaporate the solution to fumes of sulphur trioxide and proceed as described.
5. Approximately 10 g of sodium chloride should be used if more than about 250 mg of lead is present. It can be omitted if lead sulphate is absent.
6. If the diethyldithiocarbamate extraction cannot be performed the same day, allow the solution to stand overnight at this point. Addition of the EDTA-sodium hydroxide solution is not harmful except that the EDTA will precipitate from the acidic solution during prolonged standing.
7. A pH meter is only necessary for highly coloured copper and nickel solutions of low iron content. If an appreciable amount of iron is present, add 50% sodium hydroxide solution until the solution changes colour because of the formation of the reddish brown iron (III)-EDTA complex.
8. Carbon tetrachloride, instead of chloroform, is not recommended for the extraction of bismuth from solutions containing an appreciable amount of lead. Lead diethyldithiocarbamate, which is less soluble in this solvent, precipitates in the organic phase and may interfere mechanically with the extraction of bismuth.
9. Approximately two- to five-fold scale expansion is recommended for the determination of about 2 µg/mL or less of bismuth.

ACCURACY

Illustrated in Table 5 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine bismuth in molybdenum, nickel and zinc metals and alloys.

REFERENCES

1. Donaldson, E.M. "Determination of bismuth in ores, concentrates and non-ferrous alloys by atomic-absorption spectrophotometry after separation by diethyldithiocarbamate extraction or iron collection"; Talanta 26:1119-1123; 1979.

2. Idem. "Spectrophotometric determination of bismuth in concentrates and non-ferrous alloys by the iodide method after separations by diethyldithiocarbamate and xanthate extraction"; ibid 25:131-136; 1978.

SPECTROPHOTOMETRIC DETERMINATION OF BISMUTH IN COPPER METAL AND COPPER-, TIN- AND LEAD-BASE ALLOYS BY THE IODIDE METHOD AFTER SEPARATION BY DIETHYLDITHIOCARBAMATE AND XANTHATE EXTRACTIONS

PRINCIPLE

Bismuth is separated from all matrix elements, except lead and thallium, by extraction of its diethyldithiocarbamate complex at pH 11.5-12.0 from a sodium hydroxide medium containing citric acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA) and potassium cyanide as complexing agents. It is subsequently back-extracted into 12 M hydrochloric acid and separated from most of the coextracted lead and from any thallium present by chloroform extraction of its ethyl xanthate complex from a 2.5 M hydrochloric acid-tartaric acid-ammonium chloride medium. Bismuth is ultimately determined spectrophotometrically by measuring the absorbance at either 337 or 460 nm of the yellow iodobismuthite ion formed in a 1 M sulphuric acid-0.24 M potassium iodide medium in a reducing - hypophosphorous acid - environment. The molar absorptivities of the complex at these wavelengths are 3.05×10^3 and 1.12×10^3 $L.mol^{-1}.mm^{-1}$, respectively (1).

INTERFERENCES

Nickel, cobalt and chromium, which form coloured solutions; platinum, palladium, antimony and tin, which form soluble coloured compounds with iodide; lead, thallium, silver, copper and cadmium, which form insoluble iodides; and iron (III), which oxidizes iodide and liberates iodine, interfere in the determination of bismuth as the iodide (2-4). Although platinum and palladium are not usually present in copper-, tin- and lead-base alloys, interference from them and from all the above elements, except lead and thallium (III), is avoided by the preliminary separation of bismuth by chloroform extraction of its yellow diethyldithiocarbamate complex from a strongly alkaline sodium hydroxide medium - pH 11.5-12.0 - containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents. Lead and thallium (III) are partly and completely coextracted, respectively, as diethyldithiocarbamate complexes (1,5,6). Bismuth is ultimately separated from most of the coextracted lead, and from any thallium present, after it is reduced to thallium (I) with sulphurous acid, by chloroform extraction of its ethyl xanthate complex from a 2.5 M hydrochloric acid-tartaric acid-ammonium chloride medium. Small amounts of lead - less than 100 µg - that is coextracted as the xanthate does not interfere in the determination of bismuth when the absorbance measurement is made at 460 nm, but a high result is obtained if the measurement is made at 337 nm. This interference is eliminated by washing the bismuth xanthate extract with a 2.5 M hydrochloric acid solution of the same composition as the medium used for extraction (1).

In the absence of lead, zinc and particularly molybdenum cause low results for bismuth because the diethyldithiocarbamate complex is not quantitatively back-extracted from the chloroform phase into concentrated hydrochloric acid. This interference is avoided by adding lead before the extraction of bismuth diethyldithiocarbamate (1).

RANGE

This method is suitable for samples containing approximately 0.0001 to 1% of bismuth but material containing higher concentrations can also be analyzed with reasonable accuracy.

REAGENTS

STANDARD BISMUTH SOLUTION, 1 mg/mL. Prepare the solution as described in the atomic-absorption-iron collection method for bismuth (p 24). Prepare a 5-µg/mL solution by diluting 5 mL of this stock solution and 10 mL of concentrated nitric acid to 1 L with water. Prepare a 50-µg/mL solution by diluting 10 mL of the stock solution and 5 mL of concentrated nitric acid to 200 mL with

water. Prepare the diluted solutions fresh as required.

LEAD SOLUTION, 5 mg/mL. Dissolve 2.5 g of pure lead metal by heating it gently with 150 mL of 50% nitric acid, then cool the solution to room temperature and dilute it to 500 mL with water.

SODIUM HYPOPHOSPHITE SOLUTION, 15% *m/V*. Prepare the solution fresh as required.

POTASSIUM IODIDE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

TARTARIC ACID SOLUTION, 20% *m/V*.

SULPHUROUS ACID. Water saturated with sulphur dioxide.

AMMONIUM CHLORIDE SOLUTION, 25% *m/V*.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

HYDROCHLORIC ACID-TARTARIC ACID-AMMONIUM CHLORIDE WASH SOLUTION. Add 215 mL of concentrated hydrochloric acid to approximately 500 mL of water, then add 25 mL of 20% tartaric acid solution and 200 mL of 25% ammonium chloride solution and dilute the resulting solution to 1 L with water.

SULPHURIC ACID, 50% *V/V*.

NITRIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION CURVES

Add 3 mL of 50% sulphuric acid and 1 mL of concentrated nitric acid to each of thirteen 100-mL beakers; then by burette, add to the first five beakers 1, 2, 4, 6 and 8 mL, respectively, of the dilute standard 5-µg/mL bismuth solution. By burette, add to the next seven beakers 1, 2, 3, 4, 6, 8 and 10 mL, respectively, of the dilute standard 50-µg/mL bismuth solution. The contents of the last beaker constitute the blank. Evaporate each solution to fumes of sulphur trioxide and cool it to room temperature. Add 2 mL of freshly prepared 15% sodium hypophosphite solution to each beaker and mix the solutions. Add 5 mL of freshly prepared 20% potassium iodide solution, mix the solutions thoroughly, then transfer them to 25-mL volumetric flasks and dilute them to volume with water. Allow the solutions to stand for 5 min, then measure the absorbance of the blank solution and of each of the five solutions in the first series at 337 nm against water as the reference solution, using 40-mm cells. Measure the absorbance of the blank solution and of each of the seven solutions in the second series in a similar manner at 460 nm, using 10-mm cells, then measure the absorbance of the blank solution and of each of the four solutions of lowest bismuth content in the second series, using 20-mm cells. Correct the absorbance value obtained for each bismuth-iodide solution by subtracting the corresponding blank value. Plot micrograms of bismuth vs absorbance for each series of measurements.

PROCEDURE

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

Following sample decomposition (Note 1) and the ultimate adjustment of the pH of the solution to 11.75 ± 0.25 as described in the atomic-absorption-diethyldithiocarbamate extraction method for bismuth (p 27), extract bismuth as described and collect the extracts in a 125-mL separatory funnel marked at 75 mL (Note 2). Add 16 mL of concentrated hydrochloric acid to the combined extracts, close the funnel and shake it for 2 min. Allow several minutes for the layers to separate, then drain off and discard the chloroform layer. Add 2 mL each of 20% tartaric acid solution and sulphurous acid (Note 3) and 15 mL of 25% ammonium chloride solution to the resulting solution, dilute it to the 75-mL mark with water and mix it thoroughly. Add 10 mL of chloroform, then add 1 mL of freshly prepared 20% potassium ethyl xanthate solution, close the funnel and extract the solution immediately (Note 4) by shaking it for 1 min. Allow several minutes

for the layers to separate.

If the sample contains 40 µg or less of bismuth, drain the sample and blank extracts into 125-mL separatory funnels. Extract the aqueous phase three more times in a similar manner with 10-, 5- and 5-mL portions of chloroform and 1, 0.5 and 0.5 mL of xanthate solution, respectively. Add 30 mL of hydrochloric acid-tartaric acid-ammonium chloride wash solution to the combined extracts, then close the funnel and shake it for 1 min. After the layers have separated, drain the chloroform phase into a 150-mL beaker. Add 5 mL of chloroform and 0.5 mL of xanthate solution to the aqueous phase and shake the funnel for 1 min. Allow the layers to separate, then drain the chloroform phase into the beaker containing the initial extract. Extract the aqueous phase once more in a similar manner, then wash it by shaking it for about 30 s with 5 mL of chloroform. Add 10 mL of 50% nitric acid and 1 mL of concentrated perchloric acid to the combined extracts and heat the mixture in a hot water-bath to remove the chloroform. Cover the beaker, heat the solution until the evolution of oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water and evaporate the solution to fumes of sulphur trioxide or almost to dryness (Note 5). Cool the beaker, add 1 mL of 50% nitric acid and 3 mL of 50% sulphuric acid and evaporate the solution to fumes of sulphur trioxide again. Cool the solution to room temperature, then proceed with the formation of the bismuth iodide complex and the subsequent measurement of the absorbance at 337 nm as described above, using 40-mm cells. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the reagent blank solution and determine the bismuth content of the sample solution by reference to the appropriate calibration curve.

If the sample contains between 40 and 500 µg of bismuth, drain the sample and blank extracts into 150-mL beakers. Extract the aqueous phase three more times as described above, then add 10 mL of 50% nitric acid and 1 mL of concentrated perchloric acid to the combined extracts and proceed with the removal of chloroform, the ultimate formation of the bismuth iodide complex and the subsequent determination of the bismuth content of the sample solution as described above, using either 10- or 20-mm cells as required and a wavelength of 460 nm.

If the sample contains more than 500 µg of bismuth, treat the combined sample and the combined blank extract with 10 mL of 50% nitric acid and 1 mL of concentrated perchloric acid as described above and evaporate the solutions to fumes of sulphur trioxide or almost to dryness (Note 5). Cool the beakers, add 10 mL of 50% nitric acid and heat the solutions gently to dissolve the salts. Cool the solutions to room temperature, then transfer them to volumetric flasks of appropriate size - 50-200 mL -and dilute them to volume with water. Transfer a suitable identical aliquot - up to 40 mL - of each solution to 150-mL beakers and add 3 mL of 50% sulphuric acid. Evaporate the solutions to fumes of sulphur trioxide, then proceed with the complex formation and the subsequent determination of the bismuth content of the aliquot as described above, using a wavelength of 460 nm.

NOTES

1. If necessary, add sufficient lead solution during the decomposition step so that approximately 25 mg will be present. The sample can contain up to approximately 2 mg of bismuth.
2. The separatory funnel should be drained thoroughly after washing it to prevent dilution of the concentrated hydrochloric acid used for the subsequent back-extraction of bismuth.
3. The addition of sulphurous acid is not necessary if thallium is known to be absent.
4. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.
5. The small amount of sulphuric acid that is present is formed during the nitric acid oxidation of xanthate in the extract.

ACCURACY

Illustrated in Table 5 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine bismuth in molybdenum, nickel and zinc metals and alloys.

REFERENCES

1. Donaldson, E.M. "Spectrophotometric determination of bismuth in concentrates and non-ferrous alloys by the iodide method after separations by diethyldithiocarbamate and xanthate extraction"; Talanta 25:131-136; 1978.

2. Sandell, E.B. "Colorimetric determination of traces of metals" (3rd ed); New York, Interscience; 332-334; 1959.

3. Englis, D.T. and Burnett, B.B. "Determination of trace quantities of bismuth in lead and copper"; Anal Chim Acta 13:574-587; 1955.

4. Lisicki, N.M. and Boltz, D.F. "Ultraviolet spectrophotometric determination of bismuth by iodide and thiourea methods"; Anal Chem 27:1722-1724; 1955.

5. Bode, H. "Systematic studies on the use of diethyldithiocarbamates in analysis - IV: The formation of metal diethyldithiocarbamates and their extractability with respect to the pH of the solution"; Z Anal Chem 144:165-186; 1955.

6. Idem. "Systematic studies on the application of diethdithiocarbamate (DDTC) in analysis-II: Formation of metal-diethyldithiocarbamates and their extractability in dependence on the pH value of the solution"; ibid 143:182-195; 1954.

SPECTROPHOTOMETRIC DETERMINATION OF BORON IN IRON AND STEEL WITH CURCUMIN AFTER SEPARATION BY 2-ETHYL-1, 3-HEXANEDIOL-CHLOROFORM EXTRACTION

PRINCIPLE

Boron is separated from the matrix elements by chloroform extraction of the boric acid-2-ethyl-1,3-hexanediol ion-association complex from a 1 M sulphuric acid medium. It is ultimately determined spectrophotometrically, in a 1-mL portion of the extract, by measuring the absorbance at 550 nm of the red curcumin rosocyanin complex, after formation of the complex in a glacial acetic acid-concentrated sulphuric acid medium. The molar absorptivity of the complex at this wavelength is 1.65×10^{4} $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCE

The ethyl hexanediol-chloroform extraction step is highly selective and, in conjunction with zirconium as a complexing agent for fluoride, which reacts with boron to form fluoborate, separates boron from titanium, fluoride and oxidizing agents such as nitrate and hydrogen peroxide (1,2) which interfere in the formation of the curcumin complex (3,4). Both potassium hydrogen fluoride and hydrogen peroxide are used during the sample decomposition step to destroy carbides. Up to at least 500 mg of iron (III) (1) and 100 mg of tin (IV), magnesium, chromium (III), zinc, cobalt, copper (II), nickel, lead, aluminum, bismuth, vanadium (V) and phosphorus as phosphate do not interfere in the extraction of boron and are not coextracted to any significant extent (2). In the presence of 3 mL of 30% hydrogen peroxide, up to at least 50 mg each of manganese (II), titanium (IV), molybdenum (VI), tungsten (VI), niobium and tantalum also do not interfere in the extraction of boron and are not coextracted (1). Up to at least 3 M nitric acid or 2 M hydrochloric acid can be present during the extraction step (2). Aqua regia should not be present because free chlorine is coextracted and interferes during complex formation (1).

RANGE

This method is suitable for samples containing approximately 0.0001 to 0.04% of boron.

APPARATUS

APPARATUS FOR SAMPLE DECOMPOSITION. Nalgene 125-mL narrow-mouth linear (high density) polyethylene bottles fitted with air condensers. These can be made by inserting a 1-mL Nalgene pipette (inner diameter 2 mm), with its tip cut off, into a hole in a suitable size neoprene stopper so that about 40 mm of the pipette extend below the stopper.

FUNNELS FOR FILTERING THE EXTRACTS. These can be made from broken 20- or 25-mL volumetric pipettes by cutting the bulb in half.

POLYPROPYLENE SEPARATORY FUNNELS. 125-mL pear-shape type marked at 50 and 75 mL.

GRADUATED NALGENE PIPETTES. These should be used for adding all the reagents except the curcumin solution.

AUTOMATIC 500 µL PIPETTE WITH DISPOSAL PLASTIC TIPS.

REAGENTS

STANDARD BORON SOLUTION, 100 µg/mL. Dissolve 0.5715 g of pure boric acid in about 100 mL of water contained in a 250-mL plastic or teflon beaker. Transfer the solution to a 1-L volumetric flask, dilute it to volume with water, mix thoroughly and transfer the solution to a 1-L plastic bottle. Prepare a 5-µg/mL solution by diluting 10 mL of this stock solution to 200 mL with water (Note 1).

CURCUMIN SOLUTION, 0.375% *m/V*. Transfer 0.7500 g of pure curcumin to a dry (Note 2) 250-mL teflon beaker, add about 150 mL of glacial acetic acid and warm the mixture gently until the curcumin has dissolved. Transfer the solution to a dry 200-mL volumetric flask and dilute it to volume with glacial acetic acid (Note 1). This solution is stable for at least one month.

ZIRCONIUM SULPHATE SOLUTION, 20% *m/V*. Dissolve 100 g of zirconyl sulphate trihydrate ($ZrOSO_4 \cdot H_2SO_4 \cdot 3H_2O$) in about 400 mL of water containing 10 mL of 50% sulphuric acid and dilute the solution to 500 mL with water. Store the solution in a plastic bottle.

POTASSIUM HYDROGEN FLUORIDE SOLUTION, 25% *m/V*. Store the solution in a plastic bottle.

2-ETHYL-1,3-HEXANEDIOL SOLUTION. 10% *V/V* in chloroform. Dilute 50 mL of the reagent to 500 mL with chloroform in a dry glass bottle marked at 500 mL.

SODIUM CARBONATE SOLUTION, 25% *m/V*. Store the solution in a plastic bottle.

SULPHURIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

ETHYL ALCOHOL. 95%.

CALIBRATION CURVE

Add 8 mL of 50% sulphuric acid to each of seven 125-mL polypropylene separatory funnels; then by burette, add to the last six funnels 1, 2, 3, 4, 6 and 8 mL, respectively, of the dilute standard 5-µg/mL boron solution. The contents of the first funnel constitute the blank. Dilute the solutions to the 75-mL mark with water, then add 10 mL of 10% ethyl hexanediol-chloroform solution to each funnel, close it tightly and shake it for 2 min. 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 (Note 3). Extract the solution once more in a similar manner with 10 mL of ethyl hexanediol-chloroform solution, then extract it for 1 min with 3 mL of the chloroform solution. Combine these extracts with the first extract, wash the funnel containing the cotton-wool with about 2 mL of ethyl hexanediol solution and dilute the extract to volume with the same solution.

Transfer two 1-mL aliquots (Notes 4 and 5) of the blank and of each of the resulting extracts to dry 25-mL volumetric flasks (Note 3), add 1 mL of 0.375% curcumin solution (Note 4) and mix thoroughly. Using the automatic pipette, add 0.5 mL of concentrated sulphuric acid to each flask, mix the solutions thoroughly and cover the flasks with a piece of tissue. Allow the solutions to stand for 30 min to complete the complex formation, then dilute them to volume with ethyl alcohol and mix them thoroughly. Measure the absorbance of each of the resulting solutions at 550 nm against water as the reference solution using 10-mm cells. Correct the absorbance value obtained for each boron-curcumin solution by subtracting that obtained for the blank solution (Note 6). Plot micrograms of boron vs absorbance (Note 7).

PROCEDURES

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

Total boron

Transfer 0.1-0.5 g of sample containing not more than 40 µg of boron to a 125-mL Nalgene bottle (Note 8) and add 10 mL of water. Rapidly, in succession and without mixing (Note 9), add 8 mL of 50% sulphuric acid (Note 10), 3 mL of 30% hydrogen peroxide and 2 mL of 25% potassium hydrogen fluoride solution (Note 11) and immediately cap the bottle tightly with an air condenser. Place the bottle in a water-bath maintained at 60-70°C for about 2 h, then cool it to room temperature, open the cap and wash down the inside of the air condenser with a small amount of water. Add about one-quarter of a Whatman filter pulp tablet, swirl the bottle to macerate the paper, then using a plastic funnel and Whatman 11-cm No.

40 paper, filter the solution (Note 12) into a 125-mL polypropylene separatory funnel. Transfer the residue as quantitatively as possible to the filter paper (Note 13) and wash the paper and residue twice with small portions of water. Add 10 mL of 20% zirconium sulphate solution to the filtrate and close the funnel.

Transfer the paper containing the residue to a 30-mL platinum crucible, add 4 mL of 25% sodium carbonate solution (Note 14), then place the crucible in a muffle furnace and dry the paper and evaporate the solution to dryness at a low temperature. Burn off the paper at 500-600°C, then ignite and fuse the residue at about 900°C. Cool the crucible, add about 10 mL of water, then cover it with a plastic or teflon cover and carefully add 2 mL of concentrated hydrochloric acid. When the melt has dissolved (Note 15), transfer the solution to the separatory funnel containing the filtrate. Wash the crucible several times with small portions of water, dilute the resulting solution to the 75-mL mark with water and proceed with the extraction of borate, the complex formation 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 reagent blank solution and determine the boron content of the extract by reference to the calibration curve.

Acid-soluble boron

Following the decomposition of the sample and filtration of the solution to remove the acid-insoluble material as described above (Note 16), add 10 mL of 20% zirconium sulphate solution to the filtrate, dilute it to the 75-mL mark with water and proceed with the extraction and determination of boron as described above.

Acid-insoluble boron

After fusion of the insoluble material and dissolution of the melt as described above, transfer the resulting solution to a 125-mL polypropylene separatory funnel and wash the crucible thoroughly with water. Add 5 mL each of 20% zirconium sulphate solution (Note 17) and 50% sulphuric acid, dilute the solution to the 50-mL mark with water, then proceed with the extraction and subsequent determination of boron.

NOTES

1. If a Nalgene flask is not available, transfer the solution to a plastic bottle to avoid contamination from boron in glass.
2. Water should not be present because it interferes in the formation of the boron-curcumin complex (4).
3. Volumetric flasks and funnels used for the extract, and flasks ultimately used for complex formation should be washed thoroughly after use with methyl alcohol followed by distilled water and they should be kept in a drying oven until needed. When these are cooled just before use, they should be kept covered with a piece of tissue to prevent contamination from boron contained in the dust in the laboratory.
4. Use a 1-mL glass volumetric pipette and wash it with methyl alcohol after use.
5. Because of the ease with which the resulting solutions can become contaminated with dust in the laboratory, it is recommended that two aliquots of each extract should be taken for complex formation and that the mean of the two results should be used to plot calibration curve. Sample extracts should be analyzed in a similar manner. The extracts are stable for at least two weeks and can be kept in the glass flasks.
6. The absorbance of the blank varies from about 0.10-0.13 against water as the reference solution. The absorbance of the complex remains constant for at least 6 h.
7. For ease of reference when analyzing samples, plot the amount of boron added before the extraction step - not that contained in 1 mL of the ethyl hexanediol extract.
8. To avoid contamination, the Nalgene bottle and all pipettes used for adding reagents should be thoroughly washed with distilled water just before use.
9. The solution should not be mixed until the initial reaction has subsided or some may be lost through the air condenser.

10. For stainless steel, add 3 mL of concentrated hydrochloric acid at this point.
11. Potassium hydrogen fluoride is added, in conjunction with hydrogen peroxide, to decompose carbides.
12. The filtration and subsequent fusion step should be carried out even if no acid-insoluble material can be seem. A small amount dispersed throughout the sample solution is not readily visible particularly in an opaque Nalgene bottle.
13. A plastic squeeze-type wash-bottle with the tip pointed outward and upward is useful for washing any remaining residue down the inside of the Nalgene bottle while it is held over the filter funnel.
14. Sodium carbonate solution is added to neutralize any acid that may have remained on the filter paper. This could cause loss of boron by volatilization during the ignition step.
15. Any iron oxide present can be ignored. It does not interfere with the extraction of boron. However, if the crucible becomes stained with iron compounds, it should be cleaned with molten sodium carbonate before using it again.
16. If only the acid-soluble boron content of the sample is required, filtration of the solution is not necessary unless a large amount of residue is present. A small amount will not interfere with the subsequent extraction because it floats on top of the chloroform phase.
17. Zirconium solution is required to complex any fluoride ion that may have remained on the filter paper during the filtration of the residue.

ACCURACY

Illustrated in Table 6 in Appendix A.

REFERENCES

1. Donaldson, E.M. "Spectrophotometric determination of boron in iron and steel with curcumin after separation by 2-ethyl-1,3-hexanediol-chloroform extraction"; Talanta 28:825-831; 1981.

2. Agazzi, E.J. "Extraction-flame photometric determination of boron"; Anal Chem 39:233-235; 1967.

3. Mair, Jr., J.W. and Day, H.G. "Curcumin method for spectrophotometric determination of boron extracted from radiofrequency ashed animal tissues using 2-ethyl-1,3-hexanediol"; ibid 44:2015-2017; 1972.

4. Hayes, M.R. and Metcalfe, J. "The boron-curcumin complex in the determination of trace amounts of boron"; Analyst 87:956-969; 1962.

ATOMIC-ABSORPTION DETERMINATION OF CHROMIUM IN IRON, STEEL, NICKEL-COPPER ALLOYS AND ALUMINUM- AND ZIRCONIUM-BASE ALLOYS AFTER SEPARATION BY TRIBENZYLAMINE-CHLOROFORM EXTRACTION

PRINCIPLE

Chromium is separated from matrix elements by extracting chromium (VI) into chloroform containing tribenzylamine from a 0.7 M sulphuric acid medium. It is subsequently back-extracted into dilute ammonium hydroxide containing hydrogen peroxide, the solution is acidified with perchloric acid and chromium is ultimately determined by atomic-absorption spectrophotometry at 357.9 nm in a reducing air-acetylene flame in a 5% perchloric acid medium (1).

INTERFERENCES

The tribenzylamine-chloroform extraction step (1) separates chromium from iron and from many other elements that interfere in its determination in an air-acetylene flame (2-5). Only molybdenum (VI), in microgram-quantities (1), and possibly uranium (VI), platinum (IV), rhenium (VIII), niobium (V), tantalum and mercury (II) are coextracted under the conditions used for the extraction of chromium (VI) (6,7). Uranium, platinum, rhenium and mercury are not usually present in iron, steel and non-ferrous alloys. Niobium and tantalum do not interfere because they form insoluble hydrolysis compounds during the initial sample preparation step. These compounds, and any lead sulphate present, are removed by filtration before the extraction step. Possible interference from tin and antimony, which also form insoluble hydrous oxides and which may form insoluble hydrolysis compounds during the oxidation of chromium with ceric ammonium sulphate, is avoided by volatilizing them as the bromides with hydrobromic acid during the sample preparation step. Arsenic, germanium, selenium, rhenium and mercury are also removed under these conditions (1).

Manganese, in large amounts, causes a low result for chromium because it is preferentially oxidized to manganese (IV) by ceric ammonium sulphate. This uses up the cerium (IV) and prevents the complete oxidation of chromium (III) to the hexavalent state required for the extraction step. However, up to approximately 5 mg of manganese can be present in the sample or aliquot taken for extraction without causing significant error in the result. The brown manganese dioxide precipitate formed during the oxidation step can be removed by filtration before the extraction of chromium (1).

Large amounts of molybdenum and tungsten interfere in the extraction of chromium if a large amount of vanadium is present probably because of the formation of heterpoly vanadium-molybdenum and vanadium-tungsten complexes. A large amount of tungsten also causes a low result for chromium because of the formation of tungsten trioxide which occludes chromium. In the absence of vanadium, up to about 10 mg of tungsten can be present during the oxidation step without causing error in the result if the tungsten trioxide is removed by filtration before the extraction step. More than about 1 mg each of vanadium and tungsten interfere in the extraction of chromium. Up to 10 mg each of vanadium and molybdenum do not interfere if tungsten is absent. In the absence of molybdenum and tungsten, up to 100 mg of vanadium (V) will not interfere in the extraction of chromium (1).

Up to at least 10 mg of phosphorus (V), 50 mg of arsenic (V), bismuth and titanium (IV) and 100 mg of zirconium, copper (II), zinc, nickel and aluminum do not interfere in the extraction of up to 1 mg of chromium. Lead does not interfere because it does not form an insoluble chromate under the conditions employed (1).

Possible interference from perchloric acid during the atomic-absorption determination of chromium is avoided by maintaining approximately the same concentration - 5% by volume - in the

sample and calibration solutions. Because the atomic-absorption of chromium depends on its oxidation state (4,5,8) and on the ionic species (9) present in solution, the chromium in the calibration solutions must be in the same ionic form as in the sample solution. It must also be present as chromium (III), which is formed when the ammoniacal-hydrogen peroxide solution used for the back-extraction of chromium is acidified with perchloric acid. Error from these sources is avoided by treating the calibration solutions essentially the same way as the sample solution obtained after the back-extraction of chromium (1).

RANGE

This method is suitable for iron and steel containing approximately 0.001 to 5% of chromium and for nickel-copper and aluminum- and zirconium-base alloys containing approximately 0.0005 to 1% of chromium.

REAGENTS

STANDARD CHROMIUM SOLUTION, 1000 µg/mL. Dissolve 1.4147 g of pure potassium dichromate - dried at 105°C for 1 h - in water and dilute the solution to 500 mL. Prepare a 100-µg/mL solution by diluting 20 mL of this stock solution to 200 mL with water.

TRIBENZYLAMINE SOLUTION, 3% *m/V* in chloroform.

SULPHURIC ACID, 1.4 M. Dilute 160 mL of 50% sulphuric acid to 1 L with water.

AMMONIUM HYDROXIDE, 1% *V/V*.

SULPHURIC ACID, 50% *V/V*.

PERCHLORIC ACID, 50% *V/V*.

NITRIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION SOLUTIONS

Add 1 mL of 50% perchloric acid and about 30 mL of water to each of eight 100-mL beakers; then by burette, add to the first seven beakers 0.5, 1, 2, 3, 4, 5 and 6 mL, respectively, of standard 100-µg/mL chromium solution. The contents of the last beaker constitute the zero calibration solution. Add 4 drops of 30% hydrogen peroxide to each beaker, mix the solutions, then evaporate them to about 10 mL (Note 1) to destroy most of the excess of hydrogen peroxide. Cool the solutions and transfer them to 100-mL volumetric flasks containing 9 mL of 50% perchloric acid. Dilute each solution to volume with water (Note 2).

PROCEDURES

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

Iron and steel

Transfer 0.1-0.5 g of sample containing up to 5 mg of chromium and not more than about 25 mg of manganese, 50 mg of molybdenum and 5 mg each of tungsten and vanadium (Note 3) to a 250-mL teflon beaker. Cover the beaker and add 40 mL of 50% sulphuric acid and 10 mL of concentrated nitric acid. Heat the mixture gently until the sample is decomposed, then remove the cover and wash down the sides of the beaker with water. Add 2 mL of concentrated hydrofluoric acid (Note 4) and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, add 50 mL of water and heat the solution to dissolve the soluble salts. Using Whatman No. 40 paper, filter the solution into a 250-mL volumetric flask, transfer any insoluble material quantitatively to the filter paper and wash the paper 3 times with water. Reserve the beaker.

Transfer the paper containing the residue to a 30-mL zirconium crucible, burn off the paper at a low temperature and ignite the residue at about 600°C. Cool the crucible, add 0.5 g of sodium peroxide (Note 5) and fuse the mixture over an open flame. Cool the crucible and place it upright in the original beaker. Cover the beaker, add about 15 mL of water to the crucible, then carefully add 6 mL of 50% sulphuric acid. When the melt has dissolved, remove the crucible after washing it with water. Add 3 drops of concen-

trated hydrofluoric acid to the beaker and, to remove hydrogen peroxide, evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, add about 30 mL of water and heat the solution to dissolve the salts. If necessary, filter the solution - using Whatman No. 40 paper - into the volumetric flask containing the initial filtrate and wash the beaker and the paper each 3 times with water. Discard the paper and dilute the solution to volume with water.

Transfer a suitable aliquot - up to 50 mL - of the resulting solution, containing up to about 1 mg of chromium, to a 250-mL beaker and, if necessary, add sufficient 1.4 M sulphuric acid so that the total volume of the solution will be 50 mL. Add 300 mg of ceric ammonium sulphate (Note 6) to the solution, cover the beaker and, to ensure the complete oxidation of chromium, boil the solution until salts start to form or until fumes of sulphur trioxide just start to appear. Add 50 mL of water and heat the solution gently to dissolve the salts.

Cool the resulting solution and, if tungsten trioxide is present, filter the solution - using Whatman No. 42 paper - into a 250-mL separatory funnel marked at 100 mL. Wash the beaker, the paper and the precipitate thoroughly with water and dilute the solution to the mark with water. Add 10 mL of 3% tribenzylamine-chloroform solution, close the funnel and shake it for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-mL separatory funnel containing 10 mL of methyl alcohol (Note 7). Extract the aqueous phase three more times (Note 8) in a similar manner with 5-mL portions of tribenzylamine-chloroform solution. Add 25 mL of 1% ammonium hydroxide and 4 drops of 30% hydrogen peroxide to the combined extracts, then close the funnel and shake it for 1 min. After the layers have separated, drain off and discard the chloroform layer. Add 1 mL of 50% perchloric acid to the aqueous phase (Note 9), mix the solution thoroughly, then add 5 mL of chloroform and shake the funnel for about 30 s to remove the residual tribenzylamine. After the layers have separated, drain off and discard the chloroform layer. Wash the aqueous layer once more by shaking it with 5 mL of chloroform, then transfer it to a 100-mL beaker and heat the solution gently in a hot water-bath to remove the residual chloroform.

Evaporate the blank solution to about 5 mL (Note 1) to destroy most of the excess hydrogen peroxide, then transfer it to a 10-mL volumetric flask and dilute it to volume with water. Depending on the expected chromium content, evaporate the sample solution to 5-10 mL, then if necessary, add sufficient 50% perchloric acid so that 1 mL will be present for each 10 mL of final solution in excess of 10 mL (Note 10). Transfer the solution to a volumetric flask of appropriate size - 10-200 mL (Note 11) - and dilute it to volume with water.

Measure the absorbance of the resulting solutions at 357.9 nm in a reducing air-acetylene flame (Note 12). Determine the chromium contents, in milligrams, of the solutions by relating the resulting values to those obtained concurrently for calibration solutions of slightly higher and lower chromium concentrations. Correct the result obtained for the sample solution by subtracting that obtained for the reagent blank solution.

Aluminum-base, zirconium-base and nickel-copper alloys

Transfer up to 0.2 g of sample containing up to about 1 mg of chromium and not more than about 5 mg of manganese to a 250-mL teflon beaker. Cover the beaker, add 10 mL each of 50% sulphuric acid and 50% nitric acid and heat the mixture gently until the sample has dissolved. Remove the cover, wash down the sides of the beaker with water, then add 2 mL of concentrated hydrofluoric acid (Note 4) and evaporate the solution until copious fumes of sulphur trioxide are evolved (Note 13). Cool the solution, add 50 mL of water, heat the solution to dissolve the salts, then proceed with the oxidation, the extraction and the subsequent determination of chromium as described above.

NOTES

1. Chromium is lost by volatilization if the solution is evaporated to fumes of perchloric acid or to dryness.
2. The calibration solutions are stable for at least two weeks.
3. If tungsten is absent, up to 50 mg of vanadium can be present. Conversely, if vanadium is absent, up to 10 mg of tungsten can be present.
4. If tin or antimony is present, add 10 mL of concentrated hydrobromic acid at this stage.
5. Because a large amount of sodium sulphate, which is ultimately formed, inhibits the extraction of small amounts of chromium, more sodium peroxide should not be added unless a small aliquot of the final solution is used for the subsequent extraction of chromium.
6. Ceric compounds other than sulphate are not recommended. Nitrate compounds can result in the formation of nitric acid which is partly coextracted into tribenzylamine-chloroform solution (10).
7. Methyl alcohol, which has a high dielectric constant, is added to the extract to prevent the formation of colloidal aggregates - i.e., polymerization - which prevent the complete back-extraction of chromium into 1% ammonium hydroxide (1).
8. The fourth extraction is not necessary if the second extract was colourless.
9. If much chromium is present, the solution will become blue because of the formation of perchromic acid. However, this compound is unstable and the solution will soon become colourless.
10. Additional 50% perchloric acid is not required if the final volume of the solution is to be 10 mL because 1 mL is added to acidify the dilute ammoniacal solution used for the back-extraction of chromium (VI). For final sample solution volumes of 25, 50, 100 or 200 mL, add 1.5, 4, 9 or 19 mL, respectively.
11. There is a slight positive error - approximately 7% at the 10-20-µg level - associated with the determination of small amounts of chromium when the final sample solution is diluted to 10 mL. This is because of the enhancing effect of the ammonium perchlorate that is produced when the dilute ammonium hydroxide used for the back-extraction of chromium is acidified with perchloric acid. This effect is compensated for by the blank correction when the blank and sample solutions contain comparable amounts of chromium. No significant error occurs when the final sample solution is diluted to 25 mL or more. Consequently, greater accuracy will be obtained at low levels of chromium if the final solution can be diluted to 25 mL.
12. A luminous, moderately reducing air-acetylene flame is required to obtain the highest sensitivity for chromium. The height at which the beam from the hollow-cathode lamp passes through the flame is also very important (11). Therefore, after all other instrumental parameters have been set, the acetylene flow-rate and the height of the burner should be adjusted to give maximum absorbance while a solution containing chromium is aspirated into the flame. Approximately two- to five-fold scale expansion is recommended for the determination of about 2 µg/mL or less of chromium. For stability purposes, the burner should be allowed to warm up for at least 5 min before measurements are made.
13. Too much sulphuric acid should not be removed by evaporation because a concentration of about 0.7 M is required for the extraction step.

ACCURACY

Illustrated in Table 7 in Appendix A.

OTHER APPLICATIONS

This method can probably be used to determine chromium in zinc-, cobalt-, titanium- and magnesium-base alloys and metals.

REFERENCES

1. Donaldson, E.M. "Determination of chromium in ores, rocks and related materials, iron, steel and non-ferrous alloys by atomic-

absorption spectrophotometry after separation by tribenzylamine-chloroform extraction"; Talanta 27:779-786; 1980.

2. Ihnat, M. "Interferences in the determination of chromium by flame atomic absorption spectrometry"; Can J Spectrosc 23:112-125; 1978.

3. Yanagisawa, M., Suzuki, M. and Takeuchi, T. "Cationic interferences in the atomic absorption spectrophotometry of chromium"; Anal Chim Acta 52:386-389; 1970.

4. Nyagah, C.G. and Wandiga, S.O. "Interference effects of different metals in the atomic absorption spectrophotometric determination of chromium"; Z Anal Chem 296:135-139; 1979.

5. Hurlbut, J.A. and Chriswell, C.D. "Suppression of interferences by sodium sulfate in trace chromium analyses by atomic absorption spectrometry"; Anal Chem 43:465-469; 1971.

6. Zmijewska, W. "Application of tri-n-octylamine for the substoichiometric separation of chromium (VI) in activation analysis"; J Radioanal Chem 10:187-196; 1972.

7. De, A.K., Khopkar, S.M. and Chalmers, R.A. "Solvent extraction of metals"; London, Van Nostrand Reinhold; 201-211; 1970.

8. Kraft, G., Lindenberger, D. and Beck, H. "Effect of valency on the determination of chromium by flame atomic-absorption"; Z Anal Chem 282:119-121; 1976.

9. Takada, T. and Nakano, K. "Some considerations on the atomization processes of chromium salts in air-acetylene flame"; Bunseki Kagaku 28:328-330; 1979 (Chem Abstr 91: 82506k; 1979).

10. Moore, F.L. "Long chain amines: versatile acid extractants"; Anal Chem 29:1660-1662; 1957.

11. Jedrzejewska, H. and Malusecka, M. "Interference effects of some carriers on the atomic absorption of Cr, Mn, Sb, Fe, Bi and Pb in air-acetylene flame"; Chem Anal (Warsaw) 21:585-592; 1976.

ATOMIC-ABSORPTION DETERMINATION OF COBALT IN HIGH-PURITY NICKEL, MOLYBDENUM AND TUNGSTEN METALS AFTER SEPARATION BY EXTRACTION OF THE THIOCYANATE-DIANTIPYRYLMETHANE COMPLEX

PRINCIPLE

Cobalt is separated from the matrix elements by chloroform extraction of the blue cobalt thiocyanate-diantipyrylmethane ion-association complex at pH 3.25 from a citric acid medium containing thiourea and ammonium hydrogen fluoride or hydrofluoric acid as complexing agents. Cobalt is subsequently back-extracted into dilute ammonium chloride-ammonium hydroxide solution and is ultimately determined by atomic-absorption spectrophotometry at 240.7 nm in an oxidizing air-acetylene flame in a 1% hydrochloric acid medium (1,2).

INTERFERENCES

Interference from large amounts of nickel, molybdenum and tungsten is avoided by separating cobalt - and also zinc - from them by extracting it into chloroform as the thiocyanate-diantipyrylmethane ion-association complex at pH 3.25 in the presence of citric acid and thiourea as complexing agents for iron and copper, respectively, and ammonium fluoride or hydrofluoric acid as complexing agents for molybdenum (VI), tungsten (VI), titanium (IV), vanadium (V) and bismuth (1,2). In the absence of a large amount of molybdenum or tungsten, up to 5 mg of iron (III) and 10 mg each of copper (II), cadmium, lead, manganese (II), vanadium (V), zirconium, titanium (IV), bismuth, tin (IV), antimony (V), chromium (III), chromium (VI), arsenic (V) and phosphorus (V) do not interfere in the extraction of cobalt. However, larger amounts of cadmium, chromium (III) and iron (III) interfere. Cadmium interferes by reacting preferentially with diantipyrylmethane to form a colourless ion-association complex which is partly extracted into chloroform. Chromium (III) interferes because it is partly precipitated as the fluoride which causes emulsification in the chloroform phase. Iron (III) is not completely complexed with citric acid at pH 3.25 and the uncomplexed portion interferes by reacting with thiocyanate and diantipyrylmethane to form a reddish brown extractable complex which obscures the blue colour of the cobalt thiocyanate complex in the chloroform phase. This makes it difficult to determine when the extraction of cobalt is complete. At the 5-mg level, the iron (III) complex is almost completely destroyed when the solution is shaken with chloroform. Less than 100 µg of iron is coextracted into the chloroform phase when molybdenum and tungsten are absent (1).

More than 4 mg of iron (III) and 5 mg of phosphorus (V) interfere in the extraction of cobalt from solutions containing 1 g of molybdenum, while more than 3 mg of iron (III) and 0.5 mg of phosphorus (V) interfere during extraction from solutions containing 1 g of tungsten. An insoluble white phosphorus-tungsten compound is formed in tungsten solutions when 3 mg or more of phosphorus (V) is present. The solution becomes milky during the initial pH adjustment step and the compound is retained in the chloroform phase during the extraction step. More iron - up to about 1.5 mg - is extracted from molybdenum and tungsten solutions than from nickel solutions. Molybdenum and tungsten are slightly coextracted in the absence of iron and phosphorus but larger amounts are extracted in their presence probably because of heterpoly compound formation. However, the amounts of iron, molybdenum and tungsten - milligram-quantities - that are coextracted do not interfere in the subsequent determination of cobalt by atomic-absorption spectrophotometry. Up to at least 5 mg each of copper (II), vanadium (V), titanium (IV), chromium (VI) and arsenic (V) and 10 mg each of the remaining elements mentioned above do not interfere in the extraction of cobalt from molybdenum and tungsten solutions (2).

This method is not applicable to samples containing about 1 mg or more of zinc because zinc is preferentially extracted as its thiocyanate-diantipyrylmethane complex.

RANGE

This method is suitable for samples containing approximately 0.0002 to 0.1% of cobalt.

REAGENTS

STANDARD COBALT SOLUTION, 100 µg/mL. Dissolve 0.4038 g of cobaltous chloride hexahydrate ($CoCl_2.6H_2O$) in water and dilute the solution to 1 L.

DIANTIPYRYLMETHANE SOLUTION, 2% *m/V* in ethyl alcohol.

AMMONIUM CHLORIDE-AMMONIUM HYDROXIDE SOLUTION, 2.5% each *m/V* and *V/V*, respectively.

SODIUM THIOCYANATE SOLUTION, 50% *m/V*.

AMMONIUM FLUORIDE SOLUTION, 5% *m/V*.

CITRIC ACID SOLUTION, 50% *m/V*.

BORIC ACID SOLUTION, 5% *m/V*.

THIOUREA SOLUTION, 10% *m/V*.

HYDROCHLORIC ACID, 1% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION SOLUTIONS

Add 1 mL of concentrated hydrochloric acid to seven 100-mL volumetric flasks, then by burette, add to the first six flasks 0.5, 1, 2, 3, 4 and 5 mL, respectively, of the standard 100-µg/mL cobalt solution. The contents of the last flask constitute the zero calibration solution. Dilute each solution to volume with water.

PROCEDURES

Nickel metal

Transfer 1 g of sample containing up to about 1 mg of cobalt to a 150-mL beaker and add 20 mL of water and 5 mL of concentrated hydrochloric acid. Cover the beaker and warm the mixture gently, then slowly add 1-mL portions of 30% hydrogen peroxide until the sample has dissolved (Note 1). Remove the cover and evaporate the solution to dryness in a water-bath to remove hydrogen peroxide, then add 1 mL of concentrated hydrochloric acid and 20 mL of water and heat the solution gently to dissolve the salts. Add 5 mL of 5% ammonium fluoride solution and 10 mL of 50% citric acid solution and mix the solution thoroughly. Using a pH meter, adjust the pH of the solution to 3.25 ± 0.10 with concentrated ammonium hydroxide. Add 5 mL of 10% thiourea solution and 10 mL of 50% sodium thiocyanate solution, mix the solution thoroughly after each addition, then readjust the pH of the solution to 3.25 ± 0.05 (Note 2).

Transfer the resulting solution to a 125-mL separatory funnel marked at 100-mL and dilute it to the mark with water. Add 5 mL of 2% diantipyrylmethane solution, mix the solution thoroughly, then add 15 mL of chloroform, close the funnel and shake it for about 1.5 min. Allow several minutes for the layers to separate, then drain the chloroform extract into a 60-mL separatory funnel. Extract the solution two more times in a similar manner using 5 mL each of diantipyrylmethane solution and chloroform each time (Note 3), then wash the aqueous phase by shaking it for about 30 s with 5 mL of chloroform. Combine these extracts with the first extract. Add 20 mL of 2.5% ammonium chloride-2.5% ammonium hydroxide solution to the resulting extract, close the funnel and shake it for 30 s. Allow the layers to separate, then drain off and discard the chloroform layer. Transfer the aqueous layer to a 150-mL beaker, add 5 mL of concentrated hydrochloric acid, heat the solution gently to remove the residual chloroform, then evaporate it to about 15 mL. Cover the beaker, add 5 mL each of concentrated nitric and hydrochloric acids and boil the solution to destroy the ammonium salts and the organic material. Remove the cover and, without baking, gently evaporate the solution to dryness on a hot-plate (Note 4). Add 2 mL of con-

centrated hydrochloric acid and about 5 mL of water to the residue in the beaker and evaporate the solution to dryness in a water-bath. Add 10 mL of 1% hydrochloric acid and heat the solution gently to dissolve the salts. If necessary, filter the solution - using Whatman No. 40 paper - into a volumetric flask of appropriate size - 25-200 mL - and wash the beaker and the paper with 1% hydrochloric acid added from a plastic wash-bottle. Dilute the solution to volume with 1% hydrochloric acid.

Measure the absorbance of the resulting solution at 240.7 nm in an oxidizing air-acetylene flame (Note 5). Determine the cobalt content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower cobalt concentrations.

Molybdenum and tungsten metals

Transfer 0.5-1 g of powdered sample containing up to about 0.5 mg of cobalt (Note 6) to a 250-mL teflon beaker and add 5 mL of water and 4 mL of concentrated hydrofluoric acid. Cover the beaker with a teflon cover, then add 2 mL of concentrated nitric acid and heat the mixture gently until the metal has dissolved (Note 7). Slowly add 5 mL of concentrated formic acid through the lip of the beaker in about 1-mL increments to destroy the excess nitric acid, then heat the solution gently until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to about 5 mL. Add 10 mL of 50% citric acid solution and 40 mL of 5% boric acid solution, mix the solution thoroughly and allow it to stand for 15 min to ensure the complete complexation of the excess hydrofluoric acid.

Using a pH meter, adjust the pH of the resulting solution to 3.25 ± 0.10 with concentrated ammonium hydroxide, then allow the solution to cool to room temperature. Add 5 mL of 10% thiourea solution and 30 mL of 50% sodium thiocyanate solution (Note 8), mix the solution thoroughly after each addition, then readjust the pH of the solution to 3.25 ± 0.05 (Note 2). Transfer the solution to a 125-mL separatory funnel marked at 150 mL and dilute it to the mark with water. Add 5 mL of 2% diantipyrylmethane solution, mix the solution thoroughly, then add 10 mL of chloroform, close the funnel and shake it for about 1.5 min. Allow the layers to separate, then drain the chloroform extract into a 60-mL separatory funnel. Extract the solution three more times in a similar manner using 5 mL of chloroform each time and 5, 3 and 2 mL, respectively, of diantipyrylmethane solution (Note 9), then strip the cobalt from the combined extracts as described above and proceed with the destruction of the ammonium salts and the organic material and the subsequent determination of cobalt as described above.

NOTES

1. Usually 5 mL of 30% hydrogen peroxide is sufficient.
2. The pH of the solution during the extraction step must be rigidly controlled because citric acid is not an effective complexing agent for iron (III) below approximately pH 3 and cobalt is not completely extracted above pH 3.45 (1).
3. Because diantipyrylmethane is soluble in chloroform, additional solution must be added before each extraction step to complex any cobalt - and also zinc - remaining in the aqueous phase after the preceding extraction step. Complete extraction of cobalt and zinc is obtained when the blue colour of the cobalt thiocyanate complex is no longer visible in the chloroform phase. Fifteen mL of 2% diantipyrylmethane solution is usually sufficient for the complexation and subsequent extraction of up to 1 mg each of cobalt and zinc (1).
4. Excessive heating of cobalt salts results in the formation of black Co_3O_4 which is relatively insoluble in water or in dilute hydrochloric acid. This will cause a low result for cobalt if suitable precautions are not taken. This is avoided by dissolving the oxide with concentrated hydrochloric acid and then evaporating the solution to dryness in a water-bath (1,2).
5. Up to ten-fold scale expansion is recommended for the determination of small amounts of

cobalt. Zinc can also be determined in the resulting sample solution by atomic-absorption spectrophotometry (p 106). If dilution of the solution is necessary for the determination of either cobalt or zinc, dilute a suitable aliquot of the solution to an appropriate volume with 1% hydrochloric acid (1,2).

6. Because molybdenum and tungsten inhibit the extraction of the cobalt thiocyanate-diantipyrylmethane complex (Note 8), the use of samples containing up to 0.5 mg of cobalt is recommended rather than 1 mg as recommended for nickel metal (2).
7. For molybdenum solutions, add 3 mL of concentrated hydrochloric acid at this stage and heat the solution until the dark brown colour disappears and the solution becomes pale yellow.
8. Approximately a 10% sodium thiocyanate medium is required for the complete extraction of cobalt from molybdenum and tungsten solutions because of the inhibiting effect of these elements on the extraction of the cobalt thiocyanate-diantipyrylmethane complex (2).
9. Fifteen mL of 2% diantipyrylmethane solution is usually required for the complexation and extraction of up to 0.5 mg each of cobalt and zinc from molybdenum and tungsten solutions because of the inhibiting effect of these elements (Notes 6 and 8) and because they are partly coextracted, particularly in the presence of iron and phosphate (2).

ACCURACY

Illustrated in Table 8 in Appendix A.

OTHER APPLICATIONS

The method described for molybenum and tungsten metals can be used to determine cobalt in high-purity niobium and tantalum metals (2).

REFERENCES

1. Donaldson, E.M. and Rolko, V.H.E. "Determination of cobalt and zinc in nickel metal by atomic-absorption spectrophotometry after separation by simultaneous chloroform extraction of their thiocyanate-diantipyrylmethane complexes"; Mineral Sciences Division Bulletin TB 93; Mines Branch, Energy, Mines and Resources Canada; 1967.
2. Donaldson, E.M., Charette, D.J. and Rolko, V.H.E. "Determination of cobalt and zinc in high-purity niobium ,tantalum, molybdenum and tungsten metals by atomic-absorption spectrophotometry after separation by extraction"; Talanta 16:1305-1310; 1969.

SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN HIGH-PURITY MOLYBDENUM AND TUNGSTEN METALS WITH BATHOCUPROINE

PRINCIPLE

Copper is determined spectrophotometrically by measuring the absorbance at 476 nm of the yellow copper (I)-bathocuproine complex, after extraction of the complex into n-amyl alcohol from a weakly acidic - pH 5.5 - ammonium tartrate-boric acid medium containing ascorbic acid as reductant (1).

INTERFERENCES

The extraction procedure eliminates interferences from coloured ions - chromium, nickel, cobalt and vanadium. Up to at least 5 mg each of cobalt, cadmium, chromium (III), nickel, manganese (II) and zinc can be present in the aliquot taken for extraction without interfering in the determination of copper. Tartaric acid complexes and prevents iron and other elements - e.g., aluminum, titanium and chromium - from precipitating as their hydrous oxides at the pH used for the formation and subsequent extraction of the copper complex (1).

RANGE

This method is suitable for samples containing approximately 0.0005 to 0.25% of copper but material containing higher concentrations can also be analyzed if a small sample is taken.

REAGENTS

STANDARD COPPER SOLUTION, 0.2 mg/mL. Dissolve 0.1000 g of pure copper metal in 10 mL of 50% nitric acid. Add 5 mL of concentrated perchloric acid and evaporate the solution to fumes of perchloric acid. Cool the solution, dilute it to 500 mL with water and store it in a plastic bottle. Prepare a 5-µg/mL solution by diluting 5 mL of this stock solution to 200 mL with water. Prepare the diluted solution fresh as required.

BATHOCUPROINE SOLUTION, 0.002 M. Dissolve 0.18 g of 2,9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline in 250 mL of ethyl alcohol. Store the solution in a plastic bottle.

AMMONIUM TARTRATE SOLUTION, copper-free, 25% *m/V*. Dissolve 125 g of the reagent and 1 g of hydroxylamine hydrochloride (Note 1) in about 350 mL of water (Note 2) and transfer the solution to a 500-mL separatory funnel. Add 20 mL of 0.002 M bathocuproine solution, allow the solution to stand for about 1 h, then extract it 3 times with 15-mL portions of a 75% chloroform-25% n-amyl alcohol solution. Discard the extracts. Wash the solution 3 times by shaking it with about 10-mL portions of chloroform to remove the excess n-amyl alcohol. Filter the resulting solution, dilute it to about 500 mL with water and store it in a plastic bottle.

BORIC ACID SOLUTION, copper-free, 5% *m/V*. Dissolve 50 g of the reagent in about 800 mL of hot water. Cool the solution and transfer it to a 1-L separatory funnel. Add 1 g of hydroxylamine hydrochloride (Note 1), mix the solution thoroughly, then add 30 mL of bathocuproine solution and allow the solution to stand for about 5 min. Extract the solution as described above, then filter it and dilute it to 1 L with water. Store the solution in a plastic bottle.

ASCORBIC ACID SOLUTION, copper-free, 10% *m/V*. Dissolve 10 g of the reagent in about 60 mL of water, transfer the solution to a 125-mL separatory funnel, then add 5 mL of bathocuproine solution and allow the solution to stand for 5 min. Extract the solution twice with 10-mL portions of the chloroform-n-amyl alcohol solution, then wash it 3 times by shaking it with 5-mL portions of

chloroform to remove the excess n-amyl alcohol. Filter the solution and dilute it to about 100 mL with water. Prepare a fresh solution every two days.

AMMONIUM TARTRATE-BORIC ACID-ASCORBIC ACID SOLUTION. Add 20 mL each of 25% ammonium tartrate and 10% ascorbic acid solutions and 40 mL of 5% boric acid solution to a 250-mL beaker. Using a pH meter, adjust the pH of the resulting solution to 0.5 ± 0.1 with concentrated ammonium hydroxide, then transfer the solution to a 200-mL volumetric flask and dilute it to volume with water.

WATER, deionized. Prepare by passing distilled water through a column of Dowex 50W-X8 resin.

N-AMYL ALCOHOL. Reagent-grade, peroxide-free (Note 3).

CHLOROFORM. Reagent-grade.

CALIBRATION CURVE

Add 20-mL aliquots of the ammonium tartrate-boric acid-ascorbic acid (pH 5.5) solution (Note 4) to each of six 60-mL separatory funnels marked at 25 mL; then by burette, add to the last five funnels 1, 2, 3, 4, and 5 mL, respectively, of the dilute standard 5-µg/mL copper solution. The contents of the first funnel constitute the blank. Dilute each solution to the mark with water (Note 5), add 2 mL of 0.002 M bathocuproine solution, mix the solutions thoroughly and allow them to stand for 10 min to complete the complex formation. By pipette, add 10 mL of n-amyl alcohol to each funnel, then close the funnel and shake it for 2 min. Allow about 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the resulting n-amyl alcohol extracts into dry 15-mL centrifuge tubes and centrifuge them for 1 min. Measure the absorbance of each copper-bathocuproine extract (Note 6) at 476 nm against the blank extract as the reference solution, using 20-mm cells (Note 7). Plot micrograms of copper vs absorbance.

PROCEDURE

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

Transfer 0.25-0.5 g of powdered sample to a 250-mL teflon beaker and add 2 mL of concentrated hydrofluoric acid. Cover the beaker with a teflon cover, then add concentrated nitric acid slowly, about 10 drops at a time, until the metal has dissolved (Note 8). Slowly add 3 mL of concentrated formic acid through the lip of the beaker, in about 1-mL increments, to destroy the excess nitric acid, then heat the solution gently until the evolution of oxides of nitrogen ceases. Wash down the sides of the beaker with a small amount of water and evaporate the solution to about 5 mL. Add 10 mL each of water and 25% ammonium tartrate solution and heat the solution gently - without boiling - for 5-10 min (Note 9). Add 20 mL of 5% boric acid solution, mix the solution thoroughly and allow it to stand for about 20 min to ensure the complete complexation of the excess hydrofluoric acid (Note 10). Add 10 mL of 10% ascorbic acid solution to the resulting solution (Note 11), mix it thoroughly, then using a pH meter, adjust the pH of the solution to 5.5 ± 0.1 (Note 4) with concentrated ammonium hydroxide. Transfer the solution to a 100-mL volumetric flask and dilute it to volume with water (Note 12).

Transfer suitable identical 4-20-mL aliquots of the sample and blank solutions to 60-mL separatory funnels, dilute the solutions to approximately 25 mL with water and proceed with the complex formation and the subsequent extraction of the complex 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. Hydroxylamine hydrochloride is recommended as a reductant because if ascorbic acid is used the solution becomes dark yellow in about one week.
2. Deionized water should be used to prepare all

the reagents and it should be used throughout the sample preparation and subsequent steps. If iron is also to be determined (Note 4) by the bathophenanthroline method (p 49), all the solutions used should also be freed of iron as described in the above method by adding the recommended volumes of bathophenanthroline solution before the extraction step.

3. To test the n-amyl alcohol for the presence of peroxides, shake a 50-mL portion in a separatory funnel with 50 mL of 20% hydrochloric acid for 2-3 min, then add potassium iodide and iodine indicator to the acid phase. Peroxides are present if a blue colour develops on standing. The solvent can be freed of peroxides as follows:
   Using a mechanical shaker, shake about 500 mL of the solvent in a 1-L Erlenmeyer flask for 2 h with 200 mL of 10% hydrochloric acid containing about 5 g of hydroxylamine hydrochloride. Transfer the mixture to a 1-L separatory funnel and drain off the aqueous phase. Wash the n-amyl alcohol layer 4 times with about 200-mL portions of water, then filter the solvent through silicone-treated phase separating paper to remove the excess water.
4. A pH of 5.5 is recommended in this method so that iron can also be determined with bathophenanthroline (p 49) by using a suitable aliquot of the sample solution obtained as described in the procedure. If only copper is to be determined, such rigid control of the pH is not necessary. The copper-bathocuproine complex can be completely extracted from solutions of pH 1.45 to 6.25.
5. The volume of the aqueous phase before extraction should be kept relatively constant to eliminate volume changes in the extract resulting from the slight solubility of n-amyl alcohol in water - i.e., 2.19% by weight at 25°C.
6. The absorbance of the n-amyl alcohol extract of the copper-bathocuproine complex remains constant for at least three days. The apparent molar absorptivity of the complex in n-amyl alcohol at 476 nm, based on complete extraction of copper and a 10-mL volume, is 1.21×10^3 $L.mol^{-1}.mm^{-1}$.
7. The calibration curve can be extended to 50 µg of copper if 10-mm cells are used.
8. Usually 1 or 2 mL of concentrated nitric acid is sufficient. If necessary, heat the solution gently until the sample has completely dissolved. For molybdenum metal, add 2 mL of concentrated hydrochloric acid at this point and heat the solution until the dark brown colour disappears and the solution becomes pale yellow.
9. The solution should become clear after heating.
10. If the copper determination cannot be completed the same day, allow the solution to stand overnight at this point.
11. If iron (Note 4) is also to be determined by the bathophenanthroline method (p 49), add 2 mL of 50% sulphuric acid and 5 mL of 10% iron-free hydroxylamine hydrochloride solution at this stage.
12. A slightly low result - i.e., about 0.002% low at the 0.1% level - will be obtained if the sample solution is allowed to stand for more than about 2 h before the extraction and subsequent determination of copper.

ACCURACY

Illustrated in Table 9 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine copper in high-purity niobium and tantalum metals. It is probably also applicable to high-purity aluminum, magnesium, titanium and zirconium metals.

REFERENCE

1. Penner (Donaldson), E.M. and Inman, W.R. "Determination of copper in high-purity niobium, tantalum, molybdenum and tungsten metals with bathocuproine"; Talanta 10:407-412; 1963.

SPECTROPHOTOMETRIC DETERMINATION OF IRON IN HIGH-PURITY MOLYBDENUM AND TUNGSTEN METALS WITH BATHOPHENANTHROLINE

PRINCIPLE

Iron is determined spectrophotometrically by measuring the absorbance at 536 nm of the red iron (II)-bathophenanthroline complex, after extraction of the complex into n-amyl alcohol from a weakly acidic - pH 5.5 - ammonium tartrate-boric acid medium containing ascorbic acid and hydroxylamine hydrochloride as reductants (1).

INTERFERENCES

Small amounts of copper, cobalt, cadmium, nickel, zinc and manganese interfere because they also react with bathophenanthroline. In the absence of the other elements mentioned above, interference from up to 50 µg of copper can be eliminated by complexing it with thiourea before the formation of the iron complex. Up to 10 µg each of copper and the above elements can be present in the aliquot taken for extraction without causing significant error in the iron result (1).

RANGE

This method is suitable for samples containing approximately 0.0005 to 0.125% of iron but material containing higher concentrations can also be analyzed if a small sample is taken.

REAGENTS

STANDARD IRON SOLUTION, 0.2 mg/mL. Dissolve 0.1000 g of pure iron metal in 10 mL of 50% sulphuric acid, dilute the solution to 500 mL with water and store it in a plastic bottle. Prepare a 5-µg/mL iron (II) solution by diluting 5 mL of this stock solution and 1 mL of 10% ascorbic acid solution to 200 mL with water. Prepare the diluted solution fresh as required.

BATHOPHENANTHROLINE SOLUTION, 0.001 M. Dissolve 0.084 g of 4,7-diphenyl-1, 10-phenanthroline in 125 mL of ethyl alcohol and dilute the solution to 250 mL with water. Store the solution in a plastic bottle.

AMMONIUM TARTRATE SOLUTION, iron-free, 25% *m/V*. Dissolve 125 g of the reagent and 1 g of hydroxylamine hydrochloride in about 350 mL of water (Note 1) and transfer the solution to a 500-mL separatory funnel. Add 10 mL of 0.001 M bathophenanthroline solution, allow the solution to stand for about 1 h, then extract it 3 times with 15-mL portions of a 75% chloroform-25% n-amyl alcohol solution. Discard the extracts. Wash the solution 3 times by shaking it with about 10-mL portions of chloroform to remove the excess n-amyl alcohol. Filter the solution, dilute it to about 500 mL with water and store it in a plastic bottle.

BORIC ACID SOLUTION, iron-free, 5% *m/V*. Dissolve 50 g of the reagent in about 800 mL of hot water. Cool the solution and transfer it to a 1-L separatory funnel. Add 1 g of hydroxylamine hydrochloride, mix the solution thoroughly, then add 20 mL of bathophenanthroline solution and allow the solution to stand for 1 h. Extract the solution as described above, then filter it and dilute it to 1 L with water. Store the solution in a plastic bottle.

HYDROXYLAMINE HYDROCHLORIDE SOLUTION, iron-free, 10% *m/V*. Dissolve 10 g of the reagent in about 60 mL of water, transfer the solution to a 125-mL separatory funnel, then add 5 mL of bathophenanthroline solution and allow the solution to stand for 10 min. Extract the solution 3 times with 10-mL portions of the chloroform-n-amyl alcohol solution, then wash it 3 times by shaking it with 5-mL portions of chloroform to remove the excess n-amyl alcohol. Filter the solution and dilute it to 100 mL with water. Prepare a fresh solution every five days.

ASCORBIC ACID SOLUTION, 10% *m/V*. Prepare a fresh solution every two days (Note 2).

THIOUREA SOLUTION, 5% *m/V*.

AMMONIUM TARTRATE-BORIC ACID-ASCORBIC ACID-HYDROXYLAMINE HYDROCHLORIDE SOLUTION. Add 20 mL each of 25% ammonium tartrate and 10% ascorbic acid solutions, 40 mL of 5% boric acid solution and 10 mL of 10% hydroxylamine hydrochloride solution to a 250-mL beaker. Using a pH meter, adjust the pH of the resulting solution to 5.5 ± 0.1 with concentrated ammonium hydroxide, then transfer the solution to a 200-mL volumetric flask and dilute it to volume with water.

SULPHURIC ACID, 50% *V/V*.

N-AMYL ALCOHOL. Reagent-grade, peroxide-free (Note 3).

CHLOROFORM. Reagent-grade.

CALIBRATION CURVE

Add 20-mL aliquots of the ammonium tartrate-boric acid-ascorbic acid-hydroxylamine hydrochloride (pH 5.5) solution to each of six 60-mL separatory funnels marked at 25 mL; then by burette, add to the last five funnels 0.5, 1, 1.5, 2 and 2.5 mL, respectively, of the dilute standard 5-µg/mL iron (II) solution. The contents of the first funnel constitute the blank. Dilute each solution to the mark with water (Note 4), add 2 mL of 5% thiourea solution, mix the solutions thoroughly and allow them to stand for 5 min. Add 4 mL of 0.002 M bathophenanthroline solution to each funnel, mix the solutions thoroughly and allow them to stand for 15 min to complete the complex formation. By pipette, add 10 mL of n-amyl alcohol to each funnel, then close the funnel and shake it for 2 min. Allow about 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the resulting n-amyl alcohol extracts into dry 15-mL centrifuge tubes and centrifuge them for 1 min. Measure the absorbance of each iron-bathophenanthroline extract (Note 5) at 536 nm against the blank extract as the reference solution, using 20-mm cells (Note 6). Plot micrograms of iron vs absorbance.

PROCEDURE

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

Following the decomposition of 0.25-0.5 g of powdered sample and the ultimate addition of 20 mL of 5% boric acid solution as described in the spectrophotometric bathocuproine method for copper (p 47), allow the solution to stand for about 20 min to ensure the complete complexation of the excess hydrofluoric acid (Note 7). Add 2 mL of 50% sulphuric acid (Note 8), mix the solution thoroughly, then add 10 mL of 10% ascorbic acid solution and 5 mL of 10% hydroxylamine hydrochloride solution (Note 9). Mix the solution thoroughly, allow it to stand for 10 min to ensure the complete reduction of iron, then using a pH meter, adjust the pH of the solution to 5.5 ± 0.1 with concentrated ammonium hydroxide. Transfer the solution to a 100-mL volumetric flask and dilute it to volume with water (Note 10).

Transfer suitable identical 4-20-mL aliquots of the sample and blank solutions to 60-mL separatory funnels, dilute the solutions to approximately 25 mL with water and proceed with the complex formation and the subsequent extraction of the complex as described above. Measure the absorbance of the sample extract against the reagent blank extract and determine the iron content of the aliquot by reference to the calibration curve.

NOTES

1. If copper is also to be determined (Note 10) by the bathocuproine method (p 46), deionized water should be used to prepare all the reagents and it should be used thoroughout the sample preparation and subsequent steps. The solutions used should also be freed of copper as described in the above method by adding the recommended volumes of bathocuproine solution before the extraction step.
2. The iron content of this reagent is usually so low that purification of the solution is not necessary.
3. The n-amyl alcohol can be tested for the

presence of peroxides and purified as described in Note 3 (p 48) of the bathocuproine method for copper.

4. The volume of the aqueous phase before extraction should be kept relatively constant to eliminate volume changes in the extract resulting from the slight solubility of n-amyl alcohol in water - i.e., 2.19% by weight at 25°C.
5. The absorbance of the n-amyl alcohol extract of the iron-bathophenanthroline complex remains constant for at least 24 h (Note 9). The apparent molar absorptivity of the complex in n-amyl alcohol at 536 nm, based on complete extraction of iron and a 10-mL volume, is 2.03×10^3 $L.mol^{-1}.mm^{-1}$.
6. The calibration curve can be extended to 25 µg of iron if 10-mm cells are used.
7. If the iron determination cannot be completed the same day, allow the solution to stand overnight at this point.
8. This solution is added to ensure that the sample solution will be acidic enough for the complete reduction of iron.
9. Although ascorbic acid is a stronger reducing agent than hydroxylamine hydrochloride, its low solubility in n-amyl alcohol results in air-oxidation of the iron (II) in the extract - i.e., decolourization - if only ascorbic acid is used as reductant. The addition of hydroxylamine hydrochloride, which is more soluble in n-amyl alcohol, produces a stable extract.
10. Copper can also be determined in a suitable aliquot of the resulting solution by the bathocuproine method (p 46). However, the solution should not be allowed to stand for more than 2 h before the extraction of copper or a slightly low result - i.e., about 0.002% low at the 0.1% level - will be obtained (2).

ACCURACY

Illustrated in Table 10 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine iron in high-purity niobium and tantalum metals. It is probably also applicable to high-purity aluminum, magnesium, titanium and zirconium metals.

REFERENCES

1. Penner (Donaldson), E.M. and Inman, W.R. "Extraction and determination of iron as the bathophenanthroline complex in high-purity niobium, tantalum, molybdenum and tungsten metals"; Talanta 9:1027-1036; 1962.

2. Idem. "Determination of copper in high-purity niobium, tantalum, molybdenum and tungsten metals with bathocuproine"; ibid 10:407-412; 1963.

SPECTROPHOTOMETRIC DETERMINATION OF IRON IN COPPER METAL AND COPPER-BASE ALLOYS BY THE THIOCYANATE METHOD AFTER SEPARATION BY ISOPROPYL ETHER EXTRACTION

PRINCIPLE

Iron is separated from matrix elements by extracting the iron (III) chloro complex into isopropyl ether from a 7.75 M hydrochloric acid medium. Iron is back-extracted into water and subsequently determined spectrophotometrically by measuring the absorbance at 478 nm of the red iron (III)-thiocyanate complex formed in a 0.12 M hydrochloric acid-0.62 M sodium thiocyanate medium in the presence of ammonium persulphate as oxidant (1,2). The molar absorptivity of the complex at this wavelength is 1.08×10^3 $L.mol^{-1}.mm^{-1}$.

INTERFERENCES

The extraction procedure eliminates interference from coloured ions - cobalt and nickel - and manganese; from silver and mercury (I), which form insoluble thiocyanate compounds; from copper, bismuth, titanium, uranium and molybdenum, which form coloured thiocyanate compounds; from phosphate, which forms a complex with iron (III); and from mercury (II), cadmium, zinc and antimony (III), which form thiocyanate complexes that reduce the intensity of the iron-thiocyanate complex (3,4). Uranium, molybdenum and mercury are not usually present in copper metal or copper-base alloys. Antimony (V) is almost completely coextracted into isopropyl ether under the conditions used for the extraction of iron, and tin (IV) and vanadium (V) are partly coextracted (4). However, these elements do not interfere in the subsequent determination of iron (3).

RANGE

This method is suitable for samples containing approximately 0.0005 to 0.5% of iron but material containing higher concentrations can also be analyzed if a small sample is taken.

REAGENTS

STANDARD IRON SOLUTION, 0.5 mg/mL. Dissolve 0.2500 g of pure iron metal by heating it gently with 25 mL of concentrated hydrochloric acid. Cool the solution to room temperature and dilute it to 500 mL with water. Prepare 50- and 10-µg/mL solutions by diluting 10 mL of this stock solution to 100 and to 500 mL, respectively, with water. Prepare the diluted solutions fresh as required.

SODIUM THIOCYANATE SOLUTION, 50% *m/V*. Dissolve 500 g of the reagent in water, transfer the solution to a 1-L volumetric flask and dilute it to volume with water.

HYDROCHLORIC ACID, 7.75 M. Dilute 660 mL of concentrated hydrochloric acid to 1 L with water.

AMMONIUM PERSULPHATE SOLUTION, 5% *m/V*. Prepare the solution fresh as required.

ISOPROPYL ETHER. Reagent-grade.

CALIBRATION CURVES

Add 1 mL of concentrated hydrochloric acid to each of ten 100-mL volumetric flasks; then by burette, add to the first five flasks 2, 4, 6, 8 and 10 mL, respectively, of the dilute standard 10-µg/mL iron solution. By burette, add to the next four flasks 4, 6, 8 and 10 mL, respectively, of the dilute standard 50-µg/mL iron solution. The contents of the last flask constitute the blank. Dilute each solution to about 75 mL with water, add 5 mL of freshly prepared 5% ammonium persulphate solution and mix the solutions thoroughly. Add 10 mL of 50% sodium thiocyanate solution to the blank solution, dilute it to volume

with water, mix it thoroughly and measure the absorbance of the solution at 478 nm against water as the reference solution, using both 50- and 10-mm cells (Note 1). Add 10 mL of 50% sodium thiocyanate solution to the solution of lowest iron content in the first series, dilute it to volume with water and measure the absorbance of the solution in a similar manner, using 50-mm cells. Proceed in a similar manner with the formation of the iron-thiocyanate complex and the subsequent measurement of the absorbance for each of the remaining solutions in the first series. Measure the absorbance of the last solution in the first series using 10-mm cells, then proceed with the formation of the complex and the measurement of the absorbance for each of the solutions in the second series, using 10-mm cells. Correct the absorbance value obtained for each iron-thiocyanate solution by subtracting the corresponding blank value. Plot micrograms of iron vs absorbance for each series of measurements.

PROCEDURE

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

Transfer 0.5-1 g of sample to a 250-mL beaker and add 15 mL of concentrated hydrochloric acid. Cover the beaker and warm the mixture gently, then slowly add about 5-mL portions of 30% hydrogen peroxide until the sample has dissolved (Note 2). Place the beaker in a hot water-bath and evaporate the solution to dryness. Wash down the sides of the beaker with about 10 mL of concentrated hydrochloric acid, evaporate the solution to dryness again, then repeat the washing step and evaporate the solution to dryness again. Add 20 mL of 7.75 M hydrochloric acid to the beaker and, if necessary, warm the solution to dissolve the salts. Transfer the solution to a 50-mL volumetric flask, using 7.75 M hydrochloric acid added from a plastic wash-bottle to wash the beaker. Dilute the solution to volume with the same acid solution.

Transfer a 10-25-mL aliquot of the resulting solution (Note 3) to a 125-mL separatory funnel marked at 25 mL and, if necessary, dilute the solution to the mark with 7.75 M hydrochloric acid. Add 30 mL of isopropyl ether, then close the funnel and shake it for 1 min. Allow the layers to separate, then drain the lower aqueous layer into a second 125-mL separatory funnel. Wash the stem of the first funnel with 7.75 M hydrochloric acid and collect the washings in the second funnel. Wash the ether phase twice by shaking it for about 30 s each time with 10-mL portions of 7.75 M hydrochloric acid and collect the washings in the second funnel. Add 20 mL of isopropyl ether to the second funnel and extract the solution again by shaking it for 1 min. Allow the layers to separate, then drain off and discard the aqueous phase. Add the second extract to the first extract. Wash the second funnel twice with 10-mL portions of isopropyl ether and add the washings to the funnel containing the combined extracts. Wash the resulting extract twice as described above with 10-mL portions of 7.75 M hydrochloric acid and discard the washings. Add 15 mL of water to the extract, close the funnel and shake it for 30 s. Allow the layers to separate, then drain the aqueous layer into a 100-mL beaker and wash the stem of the funnel with water. Shake the ether phase two more times in a similar manner with 10-mL portions of water and add the washings to the beaker. Wash the stem of the funnel with water each time.

Heat the resulting sample and blank solutions in a hot water-bath to remove the residual ether, then evaporate them to approximately 40 mL (Note 4). Add 1 mL of concentrated hydrochloric acid to each solution, transfer them to 100-mL volumetric flasks and dilute them to about 75 mL with water. Add 5 mL of 5% ammonium persulphate solution and proceed with the formation of the iron-thiocyanate complex and the subsequent measurement of the absorbance as described above, using 10- or 50-mm cells as required. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the reagent blank solution and determine the iron content of the aliquot by reference to the appropriate calibration curve.

NOTES

1. Sodium thiocyanate solution should only be added to one solution at a time and the absorbance of the solution should be measured within several minutes because the colour of the solution, resulting from the ferric thiocyanate complex, fades on standing. This is caused by the reduction of ferric iron by thiocyanate or its decomposition products. Ammonium persulphate decreases the rate of reduction (3).
2. Usually about 20 mL of 30% hydrogen peroxide is sufficient for the decomposition of 1 g of sample. If complete decomposition cannot be obtained by this procedure, add 1 or 2 mL of concentrated nitric acid.
3. The aliquot of the sample solution should not contain more than 500 µg of iron because the whole solution obtained after the extraction step is used for complex formation. Alternatively, the final solution can be diluted to an appropriate volume with water and a suitable aliquot of the resulting solution can be used for the determination of iron.
4. At this stage, iron can also be determined by atomic-absorption spectrophotometry at 248.3 nm in an air-acetylene flame. The spectrophotometric orthophenanthroline method is not recommended if the sample contains an appreciable amount of tin because coextracted tin may interfere (1).

ACCURACY

Illustrated in Table 11 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine iron in nickel metal and alloys.

REFERENCES

1. LaRochelle, A.E., Penner (Donaldson), E.M., McMaster, C.H. and Inman, W.R. "Determination of copper, zinc, iron, nickel, tin and lead in spectrographic standard samples of brasses for the National Bureau of Standards, Washington, D.C."; Mineral Sciences Division Test Report AC-62-18; Mines Branch, Energy, Mines and Resources Canada; 1962.

2. Idem. "Analysis of brasses, bronzes and gilding metal for the National Bureau of Standards, Washington, D.C."; Mineral Sciences Division Test Report AC-63-92; Mines Branch, Energy, Mines and Resources Canada; 1963.

3. Sandell, E.B. "Colorimetric determination of traces of metals" (3rd ed); New York, Interscience; 524-530; 1959.

4. Morrison, G.H. and Freiser, H. "Solvent extraction in analytical chemistry"; New York, Wiley; 127-130; 1957.

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN HIGH-PURITY MOLYBDENUM AND TUNGSTEN METALS WITH PAN

PRINCIPLE

Molybdenum and tungsten are separated from manganese by chloroform extraction and by chloroform-isoamyl alcohol extraction of their cupferron complexes from approximately 5 and 17% sulphuric acid media, respectively. Manganese is ultimately determined spectrophotometrically by measuring the absorbance at 562 nm of the red manganese (II)-1-(2-pyridylazo)-2-naphthol (PAN) complex, after extraction of the complex into chloroform from an ammoniacal - pH 9.2 - ammonium tartrate-potassium cyanide-hydroxylamine hydrochloride medium. The molar absorptivity of the complex in chloroform at this wavelength is 4.80×10^3 $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCES

Numerous elements, including bismuth, cadmium, copper (II), tin (IV), cobalt, lead, iron (II), iron (III), nickel, zinc and vanadium (V) form extractable coloured complexes with PAN (2). In this method, large amounts of molybdenum and tungsten, some copper, and iron and any vanadium, tin, niobium, tantalum, zirconium, titanium and antimony (III) present are separated from manganese before complex formation by extracting their cupferron complexes from sulphuric acid media (3). Interference from nickel and cadmium is avoided by complexing them with potassium cyanide before the formation and extraction of the manganese-PAN complex. Up to 1 mg each of nickel, copper (II), cadmium, phosphorus (V), chromium (III), vanadium (V), aluminum, zirconium, iron (III), arsenic (V), antimony (III), antimony (V), tin (IV), titanium (IV) and bismuth can be present in the aliquot taken for analysis without causing error in the result. More than 50 µg of zinc, 100 µg of lead or 500 µg of cobalt interfere (1).

The presence of hydroxylamine hydrochloride during complex formation prevents error resulting from the air-oxidation of manganese in an ammoniacal medium (1).

RANGE

This method is suitable for samples containing approximately 0.0002 to 0.12% of manganese but material containing higher concentrations can also be analyzed if a small sample is taken.

APPARATUS

POLYPROPYLENE SEPARATORY FUNNELS. 500-mL pear-shape type.

TIMER.

REAGENTS

STANDARD MANGANESE SOLUTION, 0.2 mg/mL. Dissolve 0.1000 g of pure manganese metal in 10 mL of 50% sulphuric acid and dilute the solution to 500 mL with water (Note 1). Prepare a 2-µg/mL solution by diluting 5 mL of this stock solution to 500 mL with water. Prepare the diluted solution fresh as required.

PAN SOLUTION, 0.1% *m/V* in ethyl alcohol.

BUFFER SOLUTION. Dissolve 10 g of ammonium chloride in water and add 100 mL of concentrated ammonium hydroxide. Dissolve 1.200 g of potassium cyanide in the resulting solution, dilute the solution to 200 mL with water and store it in a plastic bottle.

AMMONIUM TARTRATE SOLUTION, 10% *m/V*.

HYDROXYLAMINE HYDROCHLORIDE SOLUTION, 20% *m/V*. Prepare a fresh solution every day.

CUPFERRON SOLUTION, 9% *m/V*. Prepare a fresh solution as required and filter it if necessary.

SULPHURIC ACID, 50% *V/V*.

HYDROCHLORIC ACID, 50% *V/V*.

WATER, deionized. Prepare by passing distilled water through a column of Dowex 50W-X8 resin.

CHLOROFORM. Reagent-grade.

ISOAMYL ALCOHOL. Reagent-grade.

CHLOROFORM-ISOAMYL ALCOHOL SOLUTION, 66 and 34% *V/V*, respectively.

CALIBRATION CURVE

Add 1 mL of 10% ammonium tartrate solution to each of seven 60-mL separatory funnels (Note 2) marked at 25 mL; then by burette, add to the first six funnels 1, 2, 3, 4, 5 and 6 mL, respectively, of the dilute standard 2-µg/mL manganese solution. The contents of the last funnel constitute the blank. Add 5 mL of 20% hydroxylamine hydrochloride solution to each funnel and dilute the resulting solutions to the mark with water (Note 3). Add 5 mL of buffer solution and 3 mL of 0.1% PAN solution to the solution of lowest manganese content and mix the solution thoroughly after each addition (Note 4). Allow exactly 45 s to elapse (Note 5), then by pipette, quickly add 10 mL of chloroform, close the funnel and shake it for 2 min. Allow about 3 min for the layers to separate, then drain off and discard the aqueous phase (Note 6). Drain the extract into a dry 15-mL centrifuge tube and close the tube with a cork. Proceed in a similar manner with the formation and the extraction of the manganese complex in each of the remaining solutions. Centrifuge each manganese-PAN extract for 30 s, then measure the absorbance of each extract (Note 7) at 562 nm against the blank extract as the reference solution, using 10-mm cells. Plot micrograms of manganese vs absorbance.

PROCEDURES

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

Molybdenum metal

Transfer 0.5 g of powdered sample to a 250-mL beaker and add 20 mL of 50% sulphuric acid. Cover the beaker and add 2 mL each of concentrated nitric and hydrochloric acids. Heat the mixture until the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool the solution, wash down the sides of the beaker with water and evaporate the solution to fumes of sulphur trioxide again to ensure the complete removal of nitric acid. Cool the solution, add about 50 mL of water and wash down the sides of the beaker with 50% hydrochloric acid added from a plastic wash-bottle (Note 8).

Cool the resulting solution to 5-10°C in an ice-bath, then transfer it to a 500-mL pyrex separatory funnel marked at 100 mL and dilute it to the mark with cold water (Note 9). Add 100 mL of cold, freshly prepared 9% cupferron solution, mix the solution thoroughly, then add 50 mL of cold chloroform, close the funnel and shake it for 1 min. Allow the layers to separate, then drain off and discard the chloroform layer. Repeat the extraction using 20 mL of cupferron solution and 25 mL of chloroform, then extract the solution three or more times using 10-mL portions of chloroform and shaking it for 1 min each time until the organic layer is colourless. Discard each extract.

Transfer the aqueous phase to a 400-mL beaker, warm it gently to remove the residual chloroform, then evaporate the solution to approximately 25 mL. Cover the beaker, add 20 mL each of concentrated hydrochloric and nitric acids, heat the solution until the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, add about 10 mL of water, wash down the sides of the beaker with 50% hydrochloric acid (Note 8) and evaporate the solution to dryness (Note 10). Cool the beaker, wash down the sides with 50% hydrochloric acid and evaporate the solution to dryness again (Note 11). Add 5 mL of 10% ammonium tartrate solution, 1 mL of concentrated hydrochloric

acid and 20 mL of water to the residue and heat the solution gently until it is clear. Dilute the resulting solution to approximately 35 mL with water, then using a pH meter, adjust the pH of the solution to 3.5 ± 0.2 (Note 12) with concentrated ammonium hydroxide. Transfer the solution to a 100-mL volumetric flask and dilute it to volume with water.

Transfer suitable identical 2-20-mL aliquots of the sample and blank solutions to 60-mL separatory funnels, dilute the solutions to approximately 25 mL with water and proceed with the complex formation and the subsequent extraction of the complex as described above. Measure the absorbance of the sample extract against the reagent blank extract and determine the manganese content of the aliquot by reference to the calibration curve.

Tungsten metal

Following the decomposition of 0.5 g of powdered sample, the removal of nitric acid with formic acid and the ultimate evaporation of the solution to about 5 mL as described in the spectrophotometric bathocuproine method for copper (p 47), add 1 mL of concentrated hydrofluoric acid and 70 mL of 50% sulphuric acid (Note 13) to the resulting solution. Wash down the sides of the beaker with 50% hydrochloric acid (Note 8) and, if necessary, warm the solution gently until it is clear. Cool the solution to 5-10°C in an ice-bath and transfer it to a 500-mL polypropylene separatory funnel marked at 100 mL. Dilute the solution to the mark with cold water, then proceed with the extraction of tungsten cupferrate as described above, using in succession 100-, 50-, 25- and three 15-mL portions of cold 66% chloroform-34% isoamyl alcohol solution (Note 14) instead of chloroform. Drain the aqueous phase into a 400-mL teflon beaker, evaporate it to about 150 mL (Note 15), then cool the solution in an ice-bath, cover the beaker and add 20 mL each of concentrated nitric and hydrochloric acids. Allow the solution to stand at room temperature until most of the organic material is decomposed, then heat the solution until the evolution of oxides of nitrogen ceases. Remove the cover and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, add about 10 mL of water and wash down the sides of the beaker with 50% hydrochloric acid. Transfer the solution to a 250-mL pyrex beaker and evaporate it to dryness (Note 10). Cool the beaker, wash down the sides with 50% hydrochloric acid, evaporate the solution to dryness again, then add the volumes of 10% ammonium tartrate solution, water and concentrated hydrochloric acid recommended above and proceed with the pH adjustment, the extraction and the subsequent determination of manganese as described above.

NOTES

1. Deionized water should be used to prepare all the reagents and it should be used throughout the sample preparation and subsequent steps.
2. The stem of each funnel should be washed with ethyl alcohol to remove water.
3. The volume of the aqueous phase before extraction should be kept relatively constant to eliminate volume changes in the extract resulting from the solubility of chloroform in water - i.e., 10 g/L at 15°C.
4. The manganese-PAN complex is not stable in solutions containing cyanide and tartrate ions. Consequently, it is necessary to work with one solution at a time and to start extracting the complex within 45-60 s (Note 5) after the addition of the PAN solution.
5. The timer should be started at the beginning of the addition of the PAN solution.
6. A low result will be obtained if the aqueous phase is allowed to remain in contact with the organic phase.
7. The absorbance of the chloroform extract of the manganese-PAN complex remains constant for at least several hours. It decreases only slightly after 24 h.
8. Trace amounts of manganese dioxide, which are not visible to the naked eye, are formed when sulphuric acid solutions of manganese (II) are evaporated to dryness. A low result will be obtained for manganese if the dioxide

adhering to the sides of the beaker is not dissolved with 50% hydrochloric acid.

9. The water, cupferron solution and chloroform should also be cooled in an ice-bath.
10. If organic material, indicated by brown or yellow salts, is still present, add 10 mL of 50% sulphuric acid and repeat the nitric acid-hydrochloric acid treatment, then evaporate the solution to dryness again.
11. At this stage, probably manganese, nickel and cobalt, depending on the amounts present, can be determined by atomic-absorption spectrophotometry if the residue is dissolved in about 1 mL of concentrated hydrochloric acid and the solution is diluted to an appropriate volume with water.
12. After the addition of 5 mL of buffer solution to an aliquot of the resulting solution, the pH of the solution during the extraction step will be approximately 9.2. The manganese-PAN complex is completely extracted in a single stage into 10 mL of chloroform in the pH range 8.8 to 9.6.
13. About a 3 M sulphuric acid solution is required for maximum extraction of tungsten into isoamyl alcohol (Note 14) as the cupferrate (4). Consequently, because of the large volume of cupferron solution required to complex the tungsten, the initial sulphuric acid concentration of the solution, after it is diluted to 100 mL with water in the separatory funnel, should be approximately 6 M.
14. Tungsten cupferrate is relatively insoluble in chloroform but it is soluble in isoamyl alcohol. Because the density of the mixture of chloroform and isoamyl alcohol is greater than 1, this mixture is recommended as extractant because it is more convenient to use than isoamyl alcohol alone when multiple extractions are required.
15. The solution will be black because of the large amount of organic material present.

ACCURACY

Illustrated in Table 12 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine manganese in high-purity niobium and tantalum metals. It is probably also applicable to high-purity titanium and zirconium metals.

REFERNCES

1. Penner (Donaldson), E.M. and Inman, W.R. "Determination of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals with PAN"; Talanta 13:489-497; 1966.

2. De, A.K., Khopkar, S.M. and Chalmers, R.A. "Solvent extraction of metals"; New York, Van Nostrand Reinhold; 120-122; 1970.

3. Idem, ibid., 104-107; 1970.

4. Allen, S.H. and Hamilton, M.B. "The estimation of molybdenum and of tungsten by dithiol"; Anal Chim Acta 7:483-493; 1952.

ATOMIC-ABSORPTION DETERMINATION OF MOLYBDENUM IN IRON AND STEEL AFTER SEPARATION BY α-BENZOINOXIME EXTRACTION OR BY α-BENZOINOXIME AND XANTHATE EXTRACTIONS

PRINCIPLE

Molybdenum is separated from matrix elements by chloroform extraction of its α-benzoinoxime complex from a 1.75 M hydrochloric acid-0.13 M tartaric acid medium. If necessary, it is subsequently separated from coextracted tungsten by chloroform extraction as the xanthate from a 1.5 M hydrochloric acid-0.13 M tartaric aid medium, after back-extraction of the molybdenum and tungsten from the chloroform phase into concentrated ammonium hydroxide. Molybdenum is ultimately determined by atomic-absorption spectrophotometry at 313.3 nm in a strongly reducing air-acetylene flame in a 15% hydrochloric acid medium containing 1000 µg/mL of aluminum as the chloride (1).

INTERFERENCES

The α-benzoinoxime extraction step separates molybdenum from many elements that interfere in its determination in both the nitrous oxide-acetylene and air-acetylene flames (2-5). Only tungsten (VI) - about 50% of the amount present - and possibly palladium (II) are coextracted under the conditions used for the extraction of molybdenum (1,6,7). The coextraction of chromium (VI) and vanadium (V) is prevented by reducing them to lower oxidation states with ferrous ammonium sulphate before the extraction step (7). Although niobium and zirconium form α-benzoinoxime complexes that are partly extracted from a dilute hydrochloric acid medium, zirconium is not coextracted in the presence of tartaric acid and niobium forms an insoluble hydrolysis compound during the sample decomposition step (1). Palladium is not usually present in iron and steel.

The presence of more than approximately 25 mg of tungsten during the α-benzoinoxime extraction step is not recommended because more tartaric acid is required to keep it in solution. This inhibits the extraction of molybdenum. Similarly, more than 1 g of tartaric acid should not be present during the xanthate extraction step because it inhibits the extraction of molybdenum xanthate. Moderate amounts of tungsten - e.g., 100 µg/mL - suppress molybdenum absorbance in an air-acetylene flame and may also interfere by precipitating in the final solution. However, the amount of tungsten that is coextracted as the α-benzoinoxime complex at the 2-mg level does not interfere in the determination of molybdenum when aluminum chloride is added to eliminate its effect, and if the volume of the final solution is 25 mL or more. Tungsten may precipitate if the volume of the solution is less. Interference from hydrochloric acid and from aluminum is avoided by maintaining the same concentrations in the sample and calibration solutions (1).

RANGE

This method is suitable for samples containing approximately 0.001 to 2.5% of molybdenum but material containing higher concentrations can also be analyzed with reasonable accuracy if a small sample is taken.

REAGENTS

STANDARD MOLYBDENUM SOLUTION, 1000 µg/mL. Dissolve 1.5000 g of pure molybdenum trioxide in 50 mL of 2% sodium hydroxide solution and dilute the solution to 1 L with water. Prepare a 100-µg/mL solution by diluting 25 mL of this stock solution to 250 mL with water. Store both solutions in plastic bottles.

ALUMINUM SOLUTION, 1% *m/V*. Dissolve 10 g of aluminum metal by heating it gently with 400 mL of 50% hydrochloric acid. Cool the solution and, if necessary, filter it - using Whatman No. 42 paper - into a 1-L volumetric flask containing

300 mL of concentrated hydrochloric acid. Dilute the resulting solution to volume with water.

α-BENZOINOXIME SOLUTION, 0.2% *m/V* in chloroform.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

FERROUS AMMONIUM SULPHATE SOLUTION, 10% *m/V*. Prepare the solution fresh as required.

BROMINE WATER.

TARTARIC ACID SOLUTION, 20% *m/V*.

PHENOLPHTHALEIN INDICATOR SOLUTION, 0.2% *m/V* in ethyl alcohol. Store the solution in a dropping bottle.

AMMONIUM HYDROXIDE, 25% *V/V*.

SODIUM HYDROXIDE SOLUTION, 50% *m/V*.

NITRIC ACID, 50% *V/V*.

SULPHURIC ACID, 50% *V/V*.

CHLOROFORM. Reagent-grade.

CALIBRATION SOLUTIONS

To eight 100-mL beakers, add, by burette, 1, 3, 5, 10, 15, 20, 25 and 30 mL, respectively, of the dilute standard 100-µg/mL molybdenum solution. Add about 10 drops of 50% sulphuric acid to each beaker and evaporate the solutions to dryness. Wash down the sides of the beakers with water and evaporate the solutions to dryness again to ensure the complete removal of sulphuric acid. Add 1 mL of 25% ammonium hydroxide, 1 drop of 0.2% phenolphthalein indicator solution and about 5 mL of water to each beaker and heat the solution gently until it is colourless. Cool the solutions, then add 10 mL each of concentrated hydrochloric acid and 1% aluminum solution and transfer the resulting solutions to 100-mL volumetric flasks. Add the same volumes of concentrated hydrochloric acid and aluminum solution to a separate flask; this constitutes the zero calibration solution. Dilute each solution to volume with water (Note 1).

PROCEDURES

Tungsten content 2 mg or less

Transfer 0.1-1 g of sample containing up to approximately 2.5 mg of molybdenum (Note 2) to a 400-mL beaker. Cover the beaker and add 10 mL each of concentrated hydrochloric acid and 50% nitric acid. Heat the mixture gently until the sample is decomposed, then remove the cover, add 4 drops of concentrated hydrofluoric acid and evaporate the solution to dryness in a hot water-bath. Add 5 mL of concentrated hydrochloric acid and 10 mL of bromine water (Note 3) and evaporate the solution to dryness again to ensure the complete removal of nitric acid.

Add 5 mL of concentrated hydrochloric acid (Note 4), 25 mL of water and 10 mL of 20% tartaric acid solution to the beaker and, if necessary, heat the solution gently to dissolve the salts. Add 50% sodium hydroxide solution in approximately 0.5-mL portions until the solution is a dark mahogany colour, then allow it to stand for several minutes to ensure the complete dissolution of any tungsten trioxide present. Add concentrated hydrochloric acid, by drops, until the solution is acidic - i.e., clear yellow, then add 15 mL in excess and, if necessary, filter the resulting solution - using Whatman No. 40 paper - into a 250-mL separatory funnel marked at 100 mL. Wash the beaker and the paper each 3 times with small portions of water, then discard the paper and residue. Add 5 mL of freshly prepared 10% ferrous ammonium sulphate solution to the funnel, dilute the solution to the mark with water and mix it thoroughly. Add 15 mL of 0.2% α-benzoinoxime-chloroform solution, close the funnel and shake it for 1 min. Allow several minutes for the layers to separate (Notes 5 and 6), then drain the chloroform phase into a 150-mL beaker. Extract the aqueous phase three more times in a similar manner with 15-mL portions of the α-benzoinoxime-chloroform solutions and add the extracts to the first extract.

Add 10 mL of 50% nitric acid to the com-

bined extracts and heat the mixture in a hot water-bath to remove the chloroform. Add 3 mL of concentrated perchloric acid and 2 mL of 50% sulphuric acid, cover the beaker and heat the solution until the evolution of oxides of nitrogen ceases. Remove the cover and evaporate the solution to dryness. Cool the solution, wash down the sides of the beaker with water and evaporate the solution to dryness again to ensure the complete removal of sulphuric acid (Note 7). Add 1 mL of 25% ammonium hydroxide (Note 8), 1 drop of 0.2% phenolphthalein indicator solution and about 3 mL of water and heat the solution gently until it is colourless (Note 9). Depending on the expected molybdenum content, add sufficient concentrated hydrochloric acid so that 1 mL will be present for each 10 mL of final solution, then add the same volume of 1% aluminum solution. Transfer the solution to a volumetric flask of appropriate size - 10-100 mL - and dilute it to volume with water.

Measure the absorbance of the resulting solution at 313.3 nm in a strongly reducing air-acetylene flame (Note 10). Determine the molybdenum content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower molybdenum concentrations.

Tungsten content approximately 2-25 mg

Collect the α-benzoinoxime-chloroform extracts (Note 11) obtained after the extraction of molybdenum as described above in a 125-mL separatory funnel (Note 12), then add 10 mL of concentrated ammonium hydroxide, close the funnel and shake it for 4 min. Allow about 5 min for the layers to separate, then drain off and discard the chloroform layer. In succession, add 5 mL of 20% tartaric acid solution, 20 mL of water and 15 mL of concentrated hydrochloric acid to the aqueous phase. Blow the resulting ammonium chloride fumes out of the funnel and allow the solution to cool to room temperature. Add 2 mL of freshly prepared 20% potassium ethyl xanthate solution (Note 13), close the funnel and mix the solution thoroughly. Allow it to stand for about 1 min to allow the formation of the reddish purple molybdenum xanthate complex, then add 10 mL of chloroform and shake the funnel for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 150-mL beaker. Extract the aqueous phase three more times in a similar manner with 10-, 5- and 5-mL portions of chloroform and 1, 0.5 and 0.5 mL, respectively, of xanthate solution (Note 14). Add 10 mL of 50% nitric acid to the combined extracts and heat the mixture in a hot water-bath to remove the chloroform. Add 3 mL of concentrated perchloric acid and 2 mL of 50% sulphuric acid and proceed with the evaporation of the solution to dryness, the dissolution of the salts in 25% ammonium hydroxide (Note 9) and the subsequent determination of molybdenum as described above.

NOTES

1. The calibration solutions should be prepared fresh every day because they are not stable on standing. It is necessary to evaporate the molybdenum solutions to dryness in the presence of sulphuric acid so that the molybdenum in the resulting calibration solutions will be present in the same ionic form as in the sample solution obtained after oxidizing a xanthate extract with nitric acid. This produces sulphuric acid.
2. For samples of high molybdenum content, up to 1 g can be taken - tungsten content 25 mg or less - if the solution ultimately obtained after the addition of 15 mL of concentrated hydrochloric acid is diluted to 100 mL with water. A suitable aliquot of the resulting solution - to which the recommended volume of ferrous ammonium sulphate solution has been added - can subsequently be diluted to approximately 100 mL in the separatory funnel with 15% hydrochloric acid-2% tartaric acid solution before the α-benzoinoxime extraction step.
3. Bromine water is added to ensure that all the molybdenum is present in the hexavalent state required for its extraction with α-benzoinoxime.
4. If tungsten is known to be absent, add 15 mL of concentrated hydrochloric acid and 10 mL

of 20% tartaric acid solution. If necessary, heat the solution gently to dissolve the salts, then proceed with the filtration step - if necessary - and the subsequent extraction of molybdenum as described.

5. The α-benzoinoxime complexes of molybdenum and tungsten are not appreciably soluble in chloroform. Consequently, if milligram-quantities of these elements are present, the chloroform phase will be cloudy or will contain flocculent white material. This does not interfere with the quantitative separation of molybdenum.
6. If the molybdenum content of the sample is so low that the final solution is to be diluted to 10 mL before the determination of molybdenum, the amount of tungsten that is coextracted at the 2-mg level may interfere by precipitating in the final solution. In this case, it is recommended that the molybdenum should be stripped from the chloroform phase and separated from the coextracted tungsten by xanthate extraction as described in the subsequent procedure.
7. If the tungsten content of the sample is not known, its presence will be indicated at this point (see also Note 11) by yellow insoluble tungsten trioxide. If an appreciable amount is present, add 0.5 mL of concentrated perchloric acid and evaporate the solution to dryness again. Add about 25 mL of water, 5 mL of 20% tartaric acid solution and 1 drop of 0.2% phenolphthalein indicator solution, then add sufficient 50% sodium hydroxide solution, by drops, until the solution is alkaline. Add concentrated hydrochloric acid, by drops, until the solution is acidic, then add 6 mL in excess and transfer the solution to a 125-mL separatory funnel marked at 50 mL. Dilute the resulting solution to the mark with water and proceed with the separation of molybdenum by extraction as the xanthate.
8. Ammonium hydroxide is required to convert tungsten to soluble ammonium tungstate.
9. From about 10-400 µg of molybdenum can be determined spectrophotometrically at this stage by the thiocyanate method. If more than 400 µg is present, transfer the solution to a 50-mL volumetric flask and dilute it to volume with water. Use a suitable aliquot - up to 20 mL - of the resulting solution for the determination of molybdenum.
10. A strongly reducing - brightly luminous, fuel-rich - air-acetylene flame is required to obtain the highest sensitivity for molybdenum. The height at which the beam from the hollow-cathode lamp passes through the flame is also extremely important (2,5). Consequently, after all other instrumental parameters have been set, the acetylene flow-rate and the height of the burner should be adjusted to give maximum absorbance while a solution containing molybdenum is aspirated into the flame. About five-fold scale expansion is recommended for the determination of about 3 µg/mL or less of molybdenum.
11. If the sample contains an appreciable amount of tungsten, the fourth extract will still be cloudy.
12. After it is washed, the separatory funnel should be drained thoroughly to prevent the dilution of the concentrated ammonium hydroxide used for the subsequent back-extraction of molybdenum.
13. The xanthate solution should be added by pipette using a suction bulb or by using a graduated or marked medicine dropper, and the extraction shold be carried out in a fume hood. Prolonged exposure to xanthate vapour can produce an allergic reaction.
14. Usually a four-stage extraction with a total volume of 4 mL of 20% potassium ethyl xanthate solution is sufficient for the separation of up to 2.5 mg of molybdenum. However, if the aqueous phase is still pink after the fourth addition of xanthate solution, continue the extraction, using 5-mL portions of chloroform and 0.5 mL of xanthate solution each time, until both the aqueous and chloroform phases are colourless.

ACCURACY

Illustrated in Table 13 in Appendix A.

REFERENCES

1. Donaldson, E.M. "Determination of molybdenum in ores, iron and steel by atomic-absorption spectrophotometry after separation by α-benzoinoxime extraction or further xanthate extraction"; Talanta 27:79-84; 1970.

2. David, D.J. "The determination of molybdenum by atomic-absorption spectrophotometry"; Analyst 86:730-740; 1961.

3. Mostyn, R.A. and Cunningham, A.F. "Determination of molybdenum in ferrous alloys by atomic absorption spectrometry"; Anal Chem 38:121-123; 1966.

4. Ramakrishna, T.V., West, P.W. and Robinson, J.W. "The determination of molybdenum by atomic absorption spectroscopy"; Anal Chim Acta 44:437-439; 1969.

5. Purushottam, A., Naidu, P.P. and Lal, S.S. "Determination of molybdenum by atomic absorption spectrophotometry"; Talanta 19:1193-1198; 1972.

6. Wish, L. "Quantitative radiochemical determination of molybdenum-99 by solvent extraction"; Anal Chem 34:625-627; 1962.

7. Peng, P.Y. and Sandell, E.B. "Simultaneous spectrophotometric determination of tungsten and molybdenum with thiocyanate after α-benzoinoxime extraction"; Anal Chim Acta 29:325-334; 1963.

SPECTROPHOTOMETRIC DETERMINATION OF NICKEL IN HIGH-PURITY MOLYBDENUM AND TUNGSTEN METALS BY CHLOROFORM EXTRACTION OF THE NICKEL (II)-DIMETHYLGLYOXIME COMPLEX

PRINCIPLE

Nickel is separated from the matrix elements by chloroform extraction of the nickel (II)-dimethylglyoxime complex at pH 6.0-6.5 from an ammonium tartrate-boric acid medium. It is ultimately determined spectrophotometrically by measuring the absorbance of the yellow extract at 370 nm (1). The molar absorptivity of the complex at this wavelength is 3.43×10^2 $L.mol^{-1}.mm^{1-}$.

INTERFERENCES

Bismuth, iron (II), cobalt (II), copper (II), palladium (II), platinum (II) and gold (III) form coloured dimethylglyoxime complexes that are partly soluble in chloroform (2). However, iron is oxidized to iron (III) during the sample decomposition step and bismuth is ultimately complexed with tartaric acid and prevented from reacting with dimethylglyoxime (1). Palladium, platinum and gold are not usually present in molybdenum and tungsten metals. Interferences from coextracted copper and cobalt, which impart a brown colour to the extract, is eliminated by stripping the complexes from the extract with dilute ammonium hydroxide (1).

Up to at least 5 mg each of copper, cobalt, chromium (III), vanadium (V) and cadmium can be present in the solution or aliquot taken for extraction without causing error in the result (1). Large amounts of manganese, zinc, magnesium, aluminum, thorium, zirconium, tin (IV), tantalum and the rare-earth elements also do not interfere (1,3).

RANGE

This method is suitable for samples containing approximately 0.0002 to 0.2% of nickel but material containing higher concentrations can also be analyzed if a small sample is taken.

REAGENTS

STANDARD NICKEL SOLUTION, 0.5 mg/mL. Dissolve 3.3647 g of nickel ammonium sulphate hexahydrate [$NiSO_4.(NH_4)_2SO_4.6H_2O$] in water and dilute the solution to 1 L. Prepare a 10-µg/mL solution by diluting 5 mL of this stock solution to 250 mL with water. Prepare the diluted solution fresh as required (Note 1).

DIMETHYLGLYOXIME SOLUTION, 1% *m/V* in ethyl alcohol.

AMMONIUM TARTRATE SOLUTION, 25% *m/V*.

BORIC ACID SOLUTION, 5% *m/V*. Dissolve 50 g of the reagent in about 800 mL of hot water. Cool the solution and dilute it to 1 L with water.

AMMONIUM HYDROXIDE, 2% *V/V*.

CHLOROFORM. Reagent-grade.

ETHYL ALCOHOL. 95%.

CALIBRATION CURVE

Add 2 mL of 25% ammonium tartrate solution to each of five 125-mL separatory funnels marked at 100 mL; then by burette, add to the last four funnels 2.5, 5, 7.5 and 10 mL, respectively, of the dilute standard 10-µg/mL nickel solution. Dilute each solution to the mark with water (Note 2). The contents of the first funnel constitute the blank. Add 5 mL each of 1% dimethylglyoxime solution and chloroform to each funnel, then close it and shake it for 2 min. Allow about 5 min for the layers to separate, then drain the chloroform extract into a 60-mL separatory funnel (Note 3). Extract the solution two more times by shaking it for 1 min with 3 mL of chloroform and then for

about 30 s with 1 mL of chloroform. Add 10 mL of 2% ammonium hydroxide to the combined extracts, then close the funnel and shake it for about 30 s (Note 4). Allow the layers to separate, then drain the chloroform layer into a dry 25-mL volumetric flask. Wash the aqueous layer by shaking it for about 30 s with 1 mL of chloroform and add this to the extract. Dilute each of the resulting extracts to volume with ethyl alcohol (Note 5). Measure the absorbance of each chloroform-ethyl alcohol solution of nickel (II) dimethylglyoximate at 370 nm against the blank solution as the reference solution, using 50-mm cells (Note 6). Plot micrograms of nickel vs absorbance.

PROCEDURE

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

Following the decomposition of 0.25-0.5 g of powdered sample (Note 7) and the ultimate addition of 20 mL of 5% boric acid solution as described in the spectrophotometric bathocuproine method for copper (p 47), allow the solution to stand for about 20 min to ensure the complete complexation of the excess hydrofluoric acid (Note 8).

If the sample contains 100 µg or less of nickel, adjust the pH of the sample and blank solutions to 6.25 ± 0.25 with concentrated ammonium hydroxide. Transfer the solutions to 125-mL separatory funnels, dilute them to approximately 100 mL with water and proceed with the extraction of nickel as described above. Measure the absorbance of the sample solution against the reagent blank solution and determine the nickel content of the sample solution by reference to the calibration curve.

If the sample contains more than 100 µg of nickel, transfer the sample and blank solutions to 100-mL volumetric flasks and dilute them to volume with water. Transfer a suitable identical 20- or 50-mL aliquot of each solution to 100-mL beakers. If 50-mL aliquots are taken, adjust the pH of each solution to 6.25 ± 0.25 with concentrated ammonium hydroxide. Transfer the resulting solutions to 125-mL separatory funnels, dilute them to approximately 100 mL with water and proceed with the extraction and the subsequent determination of the nickel content of the aliquot as described above. If 20-mL aliquots are taken, add 5 mL of 10% ammonium tartrate solution and 10 mL of 5% boric acid solution to both solutions (Note 9), then proceed with the pH adjustment and the subsequent determination of nickel as described above.

NOTES

1. If pure nickel metal is available, it can also be used to prepare the standard solution. Dissolve 0.1000 g of the metal by heating it gently with about 20 mL of 25% nitric acid, then add 5 mL of 50% sulphuric acid and evaporate the solution to dryness. Wash down the sides of the beaker with water and evaporate the solution to dryness again to ensure the complete removal of the excess acids. Dissolve the salts in water and dilute the resulting solution to 200 mL with water. If the excess acid is not removed by evaporation, the pH of the solutions used for calibration purposes may be too low (Note 2) and nickel may not be completely extracted.
2. The pH of the resulting solution will be approximately 6.5. Nickel is not completely extracted at pH values below 5.35.
3. The stem of the 60-mL funnel should be washed with ethyl alcohol to remove water.
4. In the subsequent procedure, coextracted copper and cobalt are removed from the sample extract by this washing step. Probably interference from copper - but not from cobalt - can be eliminated by complexing it with sodium thiosulphate and extracting the nickel at pH 6.5 as described in the spectrophotometric dimethylglyoxime-extraction method for copper-base alloys (p 68). However, the suitability of this procedure for eliminating interference from copper during the extraction of nickel from molybdenum and tungsten solutions has not been tested by the author. The method would not be applicable to niobium metal because nickel is not completely extracted from niobium solutions at pH values greater than 6.15.
5. Dilution of the combined chloroform extracts

with ethyl alcohol removes turbidity caused by the retention of small droplets of water in the organic phase.

6. The absorbance of the chloroform-ethyl alcohol solution of the nickel-dimethylglyoxime complex remains constant for at least 24 h.
7. It is not necessary to remove nitric acid by treating the solution with formic acid as described in the method for copper.
8. If the nickel determination cannot be completed the same day, allow the solution to stand overnight at this point.
9. Ammonium tartrate and boric acid solutions are added to increase the salt content of the solution before the extraction step. This makes it easier to adjust the pH of the solution with concentrated ammonium hydroxide because of the buffer effect of these reagents.

ACCURACY

Illustrated in Table 14 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine nickel in high-purity tantalum metal. It is also applicable to high-purity niobium metal if the pH of the solution is adjusted to 6.0 ± 0.1 before the extraction step.

REFERENCES

1. Penner (Donaldson), E.M. and Inman, W.R. "Determination of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals by chloroform extraction of nickel (II)-dimethylglyoximate"; Talanta 10:997-1003; 1963.

2. Sandell, E.B. "Colorimetric determination of traces of metals" (3rd ed); New York, Interscience; 665-681; 1959.

3. Penner (Donaldson), E.M. and Inman, W.R. "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"; Mineral Sciences Division Bulletin TB 49; Mines Branch, Energy, Mines and Resources Canada; 1963.

SPECTROPHOTOMETRIC DETERMINATION OF NICKEL IN COPPER, MAGNESIUM AND ALUMINUM METALS AND ALLOYS BY CHLOROFORM EXTRACTION OF THE NICKEL (II)-DIMETHYLGLYOXIME COMPLEX

PRINCIPLE

Nickel is separated from the matrix elements by chloroform extraction of the nickel (II)-dimethylglyoxime complex at pH 6.5 from an ammonium tartrate medium containing sodium thiosulphate as a complexing agent for copper and zinc. It is subsequently determined spectrophotometrically by measuring the absorbance of the yellow extract at 370 nm (1). The molar absorptivity of the complex at this wavelength is 3.43×10^2 L.mol^{-1}.mm^{-1}.

INTERFERENCES

The elements that form coloured dimethylglyoxime complexes that are partly soluble in chloroform are mentioned in the spectrophotometric method for determining nickel in molybdenum and tungsten metals (p 64). Interference from iron and bismuth is avoided in the same way described in the above method. Platinum, palladium and gold are not usually present in copper-, aluminum- and magnesium-base alloys.

Interference from up to about 50 mg of copper (II) is avoided by complexing it with sodium thiosulphate at pH 6.5. Copper, in larger amounts, is separated from nickel by electrolysis. Sodium thiosulphate also complexes lead, zinc, cadmium and silver under the conditions used for the extraction of nickel (1). Interference from up to 25 mg of cobalt can be eliminated by stripping the brown complex from the chloroform extract with dilute ammonium hydroxide (2).

Up to at least 500 mg each of magnesium and aluminum, 125 mg of thorium, 100 mg of iron (III), manganese (II), zinc, tin (IV), silver, zirconium and cadmium, 40 mg of cerium (IV), 10 mg of lead and 5 mg of chromium (III) and vanadium (V) can be present in the solution or aliquot taken for analysis without causing error in the nickel result (1,2).

RANGE

This method is suitable for samples containing approximately 0.0002 to 2% of nickel but material containing higher concentrations can also be analyzed if a small sample is taken.

APPARATUS

ELECTROPLATING APPARATUS WITH A MAGNETIC STIRRING MECHANISM.

REAGENTS

STANDARD NICKEL SOLUTION, 10 µg/mL. Prepare the solution as described in the spectrophotometric method for molybdenum and tungsten metals (p 64).

DIMETHYLGLYOXIME SOLUTION, 1% *m/V* in ethyl alcohol.

AMMONIUM TARTRATE SOLUTION, 20% *m/V*.

SODIUM THIOSULPHATE SOLUTION, 50% *m/V*. Dissolve 250 g of the reagent in hot water, then cool the solution and dilute it to 500 mL with water.

IRON SOLUTION, 0.05% *m/V*. Dissolve 0.25 g of pure iron metal in 25 mL of concentrated hydrochloric acid and dilute the solution to 500 mL with water.

HYDROCHLORIC ACID, 10% *V/V*.

SULPHURIC ACID, 50% *V/V*.

NITRIC ACID, 50% *V/V*.

AMMONIUM HYDROXIDE, 2% and 10% *V/V*.

AMMONIUM SULPHAMATE TABLETS (1 g).

CHLOROFORM. 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 about 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, then 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 (Note 1) marked at 100 mL and dilute them to the mark with water. Add 5 mL of chloroform and 3 mL of 1% dimethylglyoxime solution to each funnel, then close it and shake it for 2 min. Allow 5 min for the layers to separate, then carefully (Note 2) drain the chloroform extract into a dry 25-mL volumetric flask. Extract the solution two more times by shaking it for 2 min with 3 mL of chloroform and then for 30 s with 2 mL of chloroform. Dilute the combined extracts to volume with ethyl alcohol (Note 3). Measure the absorbance of each chloroform-ethyl alcohol solution of nickel (II) dimethylglyoximate at 370 nm against the blank solution as the reference solution, using 50-mm cells (Note 4). Plot micrograms of nickel vs absorbance.

PROCEDURES

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

A - Copper metal, brass and bronze (low silicon content)

(a) Nickel content 0.05% or less

Transfer 0.5 g of sample to a 300-mL electrolytic beaker, cover the beaker and add 12 mL of 50% sulphuric acid and 9 mL of 50% nitric acid. When the sample has dissolved, boil the solution gently to remove oxides of nitrogen (Notes 5 and 6), then cool the solution and dilute it to about 180 mL with water. Place a teflon-coated magnet in the beaker, then connect a clean platinum gauze cathode and a clean platinum anode to the electroplating apparatus. Lower the electrodes into the solution so that the cathode is completely covered, then cover the beaker with a split watch-glass and electrolyze the solution at a current of about 2 A and an applied potential of 4 or 5 V for about 30 min. Add a 1-g ammonium sulphamate tablet to destroy nitrous oxides and continue the electrolysis for a further 15 min (Note 7). Evaporate the resulting electrolyte until approximately 2 mL of sulphuric acid remains (Note 8), then cool the solution, add 20 mL of water and 5 mL of 20% ammonium tartrate solution and heat the solution until it is clear (Note 9). If lead sulphate is present, filter the solution - using Whatman No. 42 paper - into a 150-mL beaker and wash the electrolytic beaker and the paper thoroughly with water. Discard the paper and, if necessary, evaporate the solution to about 50 mL.

If the sample contains 100 µg or less of nickel, dilute the sample and blank solutions, if necessary, to about 50 mL with water, then using a pH meter, adjust the pH of each solution to 4.75 ± 0.25 (Note 10) with concentrated ammonium hydroxide and with 10% ammonium hydroxide as required. Add 10 mL of 50% sodium thiosulphate solution (Note 11), mix the solutions thoroughly and immediately adjust the pH of the solutions to 6.5 ± 0.1 (Note 12) using, in succession, concentrated, 10% and 2% ammonium hydroxide and, if required, concentrated and 10% hydrochloric acid. Transfer the resulting solutions to 125-mL separatory funnels, dilute them to approximately 100 mL with water and proceed with the extraction of nickel as described above (Note 13). Measure the absorbance of the sample solution against the reagent blank solution and determine the nickel content of the sample solution by reference to the calibration curve.

If the sample contains more than 100 µg of nickel, transfer the sample and blank solutions to 100-mL volumetric flasks and dilute them to volume with water. Transfer a suitable identical 20-50-mL aliquot of each solution to 150-mL beakers. If necessary, dilute the solutions to about 50 mL with water and proceed with the initial and final pH adjustments, the extraction (Note 13) and

the subsequent determination of the nickel content of the aliquot as described above.

(b) Nickel content greater than 0.05%

Following the decomposition of 0.5 g of sample as described above, boil the solution to remove oxides of nitrogen, then add 5 mL of 20% ammonium tartrate solution and, if necessary, heat the solution gently until it is clear (Note 9). If lead sulphate is present, filter the solution - using Whatman No. 42 paper - into a volumetric flask of appropriate size - 100-1000-mL - and wash the beaker and the paper thoroughly with water. Discard the paper and dilute the filtrate to volume with water. Transfer suitable identical 10-50-mL aliquots of the sample and blank solutions to 150-mL beakers and proceed with the pH adjustments, the extraction and the subsequent determination of nickel as described in Procedure A(a).

B - Silicon bronze

Transfer 0.5 g of sample to a 250-mL teflon beaker and decompose the sample as described in Procedure A(a). After the removal of oxides of nitrogen, add about 1 mL of concentrated hydrofluoric acid (Note 5) and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution and add about 25 mL of water. If less than 0.05% of nickel is present, transfer the solution to a 300-mL electrolytic beaker (Note 14) and add 2 mL of concentrated nitric acid. Dilute the solution to about 180 mL with water and proceed with the electrolysis of the solution and the subsequent determination of nickel as described in Procedure A(a). If more than 0.05% of nickel is present, add 5 mL of 20% ammonium tartrate solution and proceed with the filtration of the solution, if necessary, and the ultimate determination of nickel as described in Procedure A(b).

C - Magnesium metal and alloys

Transfer 0.5 g of sample to a 250-mL beaker and add 35 mL of water. Cover the beaker and slowly add 5 mL of concentrated hydrochloric acid. When the sample has dissolved, add 1 mL of concentrated nitric acid and boil the solution gently to remove oxides of nitrogen. Cool the solution, add 5 mL of 20% ammonium tartrate solution (Note 15), then depending on the expected nickel content, proceed with the determination of nickel as described in Procedure A(a) or A(b) (Note 16).

D - Aluminum metal and alloys

(a) Silicon content 0.7% or less

Transfer 0.5 g of sample to a 250-mL beaker, add 10 mL of water (Note 17), then cover the beaker and add 5 mL of concentrated hydrochloric acid. When the sample has dissolved, add 1 mL of concentrated nitric acid and boil the solution gently to remove oxides of nitrogen. Cool the solution, add 20 mL of 20% ammonium tartrate solution, then depending on the expected nickel content, proceed with the determination of nickel as described in Procedure A(a) or A(b) (Note 16).

(b) Silicon content greater than 0.7%

Following the decomposition of the sample as described above, add 10 mL of 50% sulphuric acid and carefully evaporate the solution to dryness to dehydrate silica. Add 30 mL of water and 2 mL of 50% sulphuric acid, heat the solution until it is clear, then using Whatman No. 40 paper containing paper pulp, filter the solution into a 250-mL beaker. Wash the beaker and the paper thoroughly with hot water.

Transfer the paper containing the residue to a 100-mL platinum dish, burn off the paper at a low temperature and ignite the residue at about 600°C. Cool the dish and add 5 mL of water, 2 mL of 50% sulphuric acid and about 10 drops of concentrated hydrofluoric acid. Add nitric acid, by drops, until all the silicon has dissolved, then evaporate the solution to dryness. Add about 5 mL of water and 5 drops of 50% sulphuric acid to the residue and add the resulting solution to the initial filtrate. If necessary, depending on the expected nickel content, evaporate the solution to about 20 mL, add 20 mL of 20% ammonium tartrate solution and proceed as described in Procedure A(a) or A(b) (Note 16).

NOTES

1. The stem of each funnel should be washed with ethyl alcohol to remove water.
2. Because of the high salt content of the aqueous phase, care must be taken that none of it accompanies the chloroform extract. This will cause the final chloroform-ethyl alcohol solution of nickel dimethylglyoximate to become turbid.
3. Dilution of the combined chloroform extracts with ethyl alcohol removes turbidity caused by the retention of small droplets of water in the organic phase.
4. The absorbance of the chloroform-ethyl alcohol solution of nickel dimethylglyoximate remains constant for at least 24 h (2).
5. If the sample contains more than about 5 mg of tin, add 10 mL each of concentrated hydrochloric and hydrobromic acids at this point and carefully evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, add about 170 mL of water and 2 mL of concentrated nitric acid and proceed as described. Arsenic and antimony are also volatilized as the bromides by this procedure.
6. If a small amount of black material is present, evaporate the solution to fumes of sulphur trioxide and proceed as described in Note 5.
7. The complete removal of copper and lead is not necessary.
8. Tin and manganese do not interfere in the extraction of nickel but they may partly precipitate as metastannic acid and manganese dioxide during the evaporation of the electrolyte. However, all the manganese dioxide and up to about 5 mg of tin will redissolve when the solution is evaporated to fumes of sulphur trioxide. Manganese dioxide in the electrolyte can also be dissolved by adding a few drops of concentrated hydrochloric acid.
9. If the solution is cloudy, add 1 mL of concentrated hydrochloric acid and continue to heat the solution until it is clear.
10. To complex zinc with sodium thiosulphate and prevent its precipitation as the hydrous oxide, the pH of the solution must be less than approximately 5.5.
11. Ten mL of 50% sodium thiosulphate solution is sufficient to complex 250 mg of zinc.
12. Nickel (II) dimethylglyoximate is extracted at pH 6.5 because the copper thiosulphate complex is stable at this pH. It is unstable above pH 7.
13. If the sample contains cobalt, coextracted cobalt must be removed from the combined extracts by shaking the resulting extract with 2% ammonium hydroxide as described in the spectrophotometric method for molybdenum and tungsten metals (p 65). However, sufficient dimethylglyoxime solution must be added to react with the cobalt and to provide an excess for the nickel. Approximately 4 mL of 1% dimethylglyoxime solution for each 5 mg of cobalt present is usually sufficient. The alcohol content of the solution - resulting from the addition of the dimethylglyoxime solution - should not exceed 35% by volume (3).
14. If lead sulphate is present, it should be removed by filtration.
15. If the sample contains a large amount of aluminum, thorium, zirconium, rare-earth elements, tin or iron, more ammonium tartrate solution may be required to complex these elements.
16. The addition of 5 mL of 50% sodium thiosulphate solution instead of 10 mL is recommended for samples of low copper and zinc contents. This amount is sufficient to complex either 50 mg of copper or about 100 mg of zinc.
17. For high-purity aluminum metal, add 10 mL of 0.5% iron solution instead of water. This hastens the dissolution process.

ACCURACY

Illustrated in Tables 15 and 16 in Appendix A.

OTHER APPLICATIONS

With modifications in the decomposition procedure, this method can be used to determine nickel in iron and steel (4).

REFERENCES

1. Penner (Donaldson), E.M. and Inman, W.R. "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"; Minerals Sciences Division Bulletin TB 49; Mines Branch, Energy, Mines and Resources Canada; 1963.

2. Idem. "Determination of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals by chloroform extraction of nickel (II) dimethylglyoximate"; Talanta 10:997-1003; 1963.

3. Sandell, E.B. "Colorimetric determination of traces of metals" (3rd ed); New York, Interscience; 671; 1959.

4. Reference 3, p 676.

SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM IN COPPER METAL AND ALLOYS WITH 3,3'-DIAMINOBENZIDINE AFTER SEPARATION BY XANTHATE EXTRACTION

PRINCIPLE

Selenium is separated from matrix elements by chloroform extraction of selenium (IV) xanthate from a 4 M hydrochloric acid-5 M sulphuric acid medium. It is ultimately determined spectrophotometrically by measuring the absorbance at 420 nm of the yellow selenium (IV)-3,3'-diaminobenzidine complex after extraction of the complex into toluene at pH 6.6-6.9 from an ethylenediaminetetraacetic acid (EDTA)-tartaric acid medium (1).

INTERFERENCES

Up to about 0.8 mg of copper at about the 200-mg level and microgram-quantities of iron, nickel, zinc and lead are coextracted as ethyl xanthate complexes under the conditions used for the extraction of selenium xanthate. Copper xanthate is not appreciably soluble in chloroform and some of the insoluble yellow compound may be retained in the chloroform phase during the extraction step, but this does not interfere in the extraction of selenium xanthate. None of the above coextracted elements interfere during complex formation (1). Interference from iron (III) and copper (II), which oxidize diaminobenzidine, is eliminated by complexing them with EDTA before complex formation (2).

Molybdenum, tellurium (IV), gold (III), platinum (IV) and palladium (II) are also partly coextracted as xanthates (3) but they are not usually present in copper-base alloys. Up to 30 mg of molybdenum and 500 µg of tellurium do not interfere during complex formation, but 500 µg of gold or platinum interfere by oxidizing diaminobenzidine; this causes a low result for selenium. Palladium - 500 µg - also causes a low result for selenium because it forms a white precipitate that produces emulsification in the toluene phase. However, up to at least 100 µg each of gold and platinum and 50 µg of palladium do not interfere.

Up to at least 500 mg of nickel, zinc and copper, 300 mg of molybdenum, 50 mg of chromium, bismuth and manganese, 25 mg of vanadium and 20 mg of tin and arsenic can be present during the extraction step without causing error in the selenium result. More than 5 mg of antimony causes a low result for selenium because it is appreciably coextracted as the antimony (V) chloro-complex from a 4 M hydrochloric acid medium (3). This results in the formation of an insoluble compound when the extract is treated with nitric and perchloric acids and the solution is ultimately evaporated to fumes of perchloric acid to remove nitric acid (1).

RANGE

This method is suitable for samples containing approximately 0.0001 to 0.2% of selenium.

REAGENTS

STANDARD SELENIUM SOLUTION, 0.1 mg/mL. Dissolve 0.1000 g of pure selenium metal by heating it gently with 25 mL of concentrated nitric acid, then cool the solution and dilute it to 1 L with water. Prepare a 10-µg/mL solution by diluting 10 mL of this stock solution to 100 mL with water. Prepare the diluted solution fresh as required.

3,3'-DIAMINOBENZIDINE TETRAHYDROCHLORIDE SOLUTION, 0.2% *m/V*. Prepare the solution just before use (Note 1).

HYDROCHLORIC ACID-SULPHURIC ACID SOLUTION, 4 M and 5 M, respectively. Add 280 mL of concentrated sulphuric acid - slowly and while stirring - to about 350 mL of water. Allow the solution to cool to room temperature, then add sufficient 0.5% potassium permanganate solution to oxidize any reducing impurities present. Add 340 mL of concentrated hydrochloric acid and dilute the solution to 1 L with water.

TARTARIC ACID SOLUTION, 20% *m/V*.

EDTA, DISODIUM SALT SOLUTION, 4% *m/V*.

FORMIC ACID, 10% *V/V*.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

AMMONIUM HYDROXIDE, 50% *V/V*.

NITRIC ACID, 50% *V/V*.

SULPHURIC ACID, 50% *V/V*.

PERCHLORIC ACID, 5% *V/V*.

TOLUENE. Reagent-grade.

CHLOROFORM. Reagent-grade.

CALIBRATION CURVES

Add 2 mL of concentrated perchloric acid to each of seven 100-mL beakers; then by burette, add to the last six beakers 0.5, 1, 2.5, 5, 7.5 and 10 mL, respectively, of the dilute standard 10-µg/mL selenium solution. The contents of the first beaker constitute the blank. Except for the blank, evaporate each solution until fumes of perchloric acid appear (Note 2), then wash down the sides of the beakers with water and evaporate the solutions just to fumes of perchloric acid again to ensure the complete removal of nitric acid. Cool the solutions to room temperature, then add 1 mL of 20% tartaric acid solution, 5 mL of 4% EDTA solution and 2 mL of 10% formic acid to each beaker and dilute the solutions to approximately 25 mL with water. Using a pH meter, adjust the pH of each solution to 1.25 ± 0.05 with 50% ammonium hydroxide. Add 5 mL of freshly prepared 0.2% 3,3'-diaminobenzidine solution, mix the solutions thoroughly and allow them to stand for 45 min to complete the complex formation. Adjust the pH of each of the resulting solutions to 6.75 ± 0.15 with 50% ammonium hydroxide and with 5% perchloric acid, if required (Note 3).

Transfer the solutions to 125-mL separatory funnels marked at 50 mL and dilute them to the mark with water. By pipette, add 20 mL of toluene to each funnel, then close it and shake it for 2 min. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layer. Drain the resulting toluene layers into dry 40-mL centrifuge tubes and centrifuge them for 1 min. Measure the absorbance of the blank extract and of each of the four extracts of lowest selenium content (Note 4) at 420 nm against toluene as the reference solution, using 40-mm cells. Measure the absorbance of the blank extract and of each of the five extracts of highest selenium content in a similar manner using 20-mm cells. Correct the absorbance value obtained for each selenium-3,3'-diaminobenzidine extract by subtracting the corresponding blank value. Plot micrograms of selenium 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 sample (Note 5) to a 250-mL beaker, then cover the beaker and add 20 mL of 50% nitric acid. When the sample has dissolved, add 30 mL of 50% sulphuric acid and heat the solution until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and carefully evaporate the solution until fumes of sulphur trioxide just start to appear (Note 6). Cool the solution, wash down the sides of the beaker with water and, to ensure the complete removal of nitric acid, evaporate the solution again until fumes of sulphur trioxide just appear. Cool the solution, add 20 mL of water and 17 mL of concentrated hydrochloric acid and boil the solution gently for about 5 min (Note 7). Cool the solution to room temperature and, if necessary, filter it - using glass fibre filter paper (Note 8) - into a 125-mL separatory funnel. Wash the beaker 3 times with 4 M hydrochloric acid-5 M sulphuric acid added from a plastic wash-bottle, then wash the paper and the residue 4 times with the same mixed acid solution. Discard the paper.

Add 10 mL of chloroform to the resulting

solution, then add 1 mL of freshly prepared 20% potassium ethyl xanthate solution (Note 9). Close the funnel and shake it for 1 min. Allow at least 5 min for the layers to separate, then drain the chloroform phase into a 125-mL separatory funnel. Extract the aqueous phase two more times in a similar manner with 10-mL portions of chloroform and 1 and 0.5 mL of xanthate solution, respectively, then wash it by shaking it for about 30 s with 5 mL of chloroform. Add 30 mL of water to the combined extracts, close the funnel and shake it for 1 min (Note 10). Allow several minutes for the layers to separate, then drain the chloroform phase into a 150-mL beaker. Add 5 mL of chloroform and 0.5 mL of xanthate solution to the aqueous wash phase, then close the funnel and shake it for 1 min. After the layers have separated, drain the chloroform layer into the beaker containing the initial extract. Wash the aqueous phase twice by shaking it for about 30 s each time with about 3 mL of chloroform and add the washings to the beaker containing the extract. Add 10 mL of 50% nitric acid and 2 mL of concentrated perchloric acid to the resulting extract and heat the mixture in a hot water-bath to remove the chloroform. Cover the beaker, heat the solution until the evolution of oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water and evaporate the solution just to fumes of perchloric acid (Note 2). Cool the solution and wash down the sides of the beaker with water. Evaporate the solution to fumes of perchloric acid again to ensure the complete removal of nitric acid, then cool it to room temperature.

If the sample contains 100 µg or less of selenium, add the recommended volumes of tartaric acid, EDTA and formic acid solutions to the sample and blank solutions, then proceed with the pH adjustment (Note 3), the formation and the extraction of the selenium (IV)-3,3'-diaminobenzidine complex and the subsequent measurement of the absorbance as described above, using 20- or 40-mm cells as required. Correct the absorbance value obtained for the sample extract by subtracting that obtained for the reagent blank extract and determine the selenium content of the sample extract by reference to the appropriate calibration curve.

If the sample contains more than 100 µg of selenium, add 3 mL of concentrated perchloric acid and 2.5 mL of 20% tartaric acid solution to the sample and blank solutions, then transfer them to volumetric flasks of appropriate size - 50 or 100 mL - and dilute them to volume with water. Transfer a suitable identical aliquot - up to 20 mL - of each solution to 100-mL beakers and, if necessary, add sufficient concentrated perchloric acid and 20% tartaric acid solution so that 2 mL and 1 mL, respectively, will be present (Note 11). Add the recommended volumes of EDTA and formic acid solutions and proceed with the pH adjustment, the complex formation and the subsequent determination of the selenium content of the aliquot as described above.

NOTES

1. A freshly prepared solution of 3,3'-diaminobenzidine must be used for complex formation because aqueous solutions of the reagent are unstable at room temperature and will rapidly turn dark red on standing (2).
2. Prolonged fuming or evaporation of the solution to dryness will cause a low result for selenium (4,5).
3. If EDTA precipitates during the time required for complex formation, difficulty will be experienced in adjusting the pH of the solution to 6.75 ± 0.15 until the precipitate has dissolved. If this occurs, adjust the pH of the solution to 7.25 ± 0.25 and swirl the beaker until the precipitate dissolves, then adjust the pH to the recommended value with 5% perchloric acid.
4. The absorbance of the toluene extract of the selenium-diaminobenzidine complex remains constant for at least 24 h (2).
5. A larger sample is not recommended because of the high metal ion content of the solution. This may result in the formation of sulphate salts that are not completely soluble in the strongly acidic hydrochloric acid-sulphuric acid medium used for the extraction of selenium xanthate.

6. Prolonged fuming of the solution results in an appreciable loss of selenium by volatilization. At this and subsequent stages, the evaporation of the solution should be discontinued as soon as fumes of sulphur trioxide appear. It is emphasized that this is the predominant source of operator error in this method.
7. Boiling the solution ensures that all the selenium is present in the tetravalent state required for its extraction as the xanthate. Selenium (VI) is reduced to selenium (IV) by chloride ion.
8. Filtration of the solution through ordinary filter paper is not recommended. Enough carbonaceous material is dissolved by the strongly acidic solution to cause some reduction of selenium to the elemental state, particularly if the solution is allowed to stand for some time before the extraction of selenium xanthate. Some lead chloride may pass through the filter paper but this does not interfere with the extraction of selenium.
9. The xanthate solution should be added by pipette using a suction bulb or by using a graduated or marked medicine dropper and the extraction should be carried out in a fume hood. Prolonged exposure to xanthate vapour can produce an allergic reaction.
10. The extract is washed with water to remove coextracted hydrochloric acid. If this is not done, some selenium will be lost by volatilization in the subsequent part of the procedure.
11. The selenium (IV)-diaminobenzidine piazselenol is not completely extracted into toluene under the proposed conditions (2). Consequently, to avoid error resulting from differences in the final salt content of the aqueous phase during extraction - which affects the degree of extraction - the concentrations of perchloric and tartaric acids in the sample solution should be approximately the same as the concentrations of these acids in the solutions used for calibration purposes.

ACCURACY

Illustrated in Table 17 in Appendix A.

REFERENCES

1. Donaldson, E.M. "Spectrophotometric determination of selenium in concentrates and high-purity copper metal with 3,3'-diaminobenzidine after separation by xanthate extraction"; Talanta 24:441-445; 1977.

2. Cheng, K.L. "Determination of traces of selenium: 3,3'-diaminobenzidine as selenium (IV) organic reagent"; Anal Chem 28:1738-1742; 1956.

3. Donaldson, E.M. "Chloroform extraction of metal ethyl xanthates from hydrochloric acid media"; Talanta 23:411-416; 1976.

4. Stanton, R.E. and MacDonald, A.J. "The determination of selenium in soils and sediments with 3,3'-diaminobenzidine"; Analyst 90:497-499; 1965.

5. Bock, R., Jacob, D., Mohamed, F. and Frankenfeld, K. "Determination of traces of selenium"; Z Anal Chem 200:81-134; 1964.

SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN COPPER METAL AND ALLOYS BY N-AMYL ALCOHOL EXTRACTION OF α-SILICOMOLYBDIC ACID

PRINCIPLE

Silicon is separated from the matrix elements by n-amyl alcohol extraction of α-silicomolybdic acid, formed at pH 2 by heating the 8 acid, from a 1.5 M sulphuric acid medium. It is subsequently determined spectrophotometrically by measuring the absorbance of the yellow extract at 350 nm (1).

INTERFERENCES

Phosphorus (V), arsenic (V) and germanium form similar yellow extractable heteropoly molybdate complexes under the conditions used for the formation of the yellow α-silicomolybdic acid complex (2). Germanium is not usually present in copper metal or alloys, and interference from up to 500 µg of either phosphorus or arsenic - but not both - is eliminated by adjusting the sulphuric acid concentration of the solution to 1.5 M before the extraction of the silicon complex; this destroys the phosphorus and arsenic complexes (1).

The extraction procedure eliminates interference from coloured ions - i.e., copper (II), iron (III), nickel and cobalt. Up to at least 300 µg each of phosphorus (V) and arsenic (V), 200 µg of iron (III) and 6 mg of aluminum can be present in the aliquot taken for extraction without causing error in the silicon result (1).

RANGE

This method is suitable for samples containing approximately 0.0003 to 0.04% of silicon but material containing higher concentrations can also be analyzed if a small sample is taken.

REAGENTS

STANDARD SILICON SOLUTION, 0.2 mg/mL. Transfer 0.2139 g of pure powdered silicon dioxide - dried at 110°C for 1 h - to a 30-mL platinum crucible, add 2 g of sodium carbonate and mix thoroughly. Cover the crucible and carefully fuse the mixture over a blast burner for about 10 min or until a clear melt is obtained. Cool the crucible and the cover, then transfer them to a 400-mL teflon beaker (Note 1) containing about 200 mL of water. Heat the solution gently to dissolve the melt, then remove the crucible and the cover after washing them thoroughly with water. Transfer the solution to a 500-mL volumetric flask, dilute it to volume with water and store the resulting solution in a plastic bottle. Prepare a 10-µg/mL solution by diluting 10 mL of this stock solution to 200 mL with water. Prepare the diluted solution fresh as required.

AMMONIUM MOLYBDATE SOLUTION, 8% *m/V*. Dissolve 40 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in water and dilute the solution to 500 mL. Store the solution in a plastic bottle.

BORIC ACID SOLUTION, 5% *m/V*. Dissolve 50 g of the reagent in about 800 mL of hot water. Cool the solution, dilute it to 1 L with water and store the resulting solution in a plastic bottle.

AMMONIUM HYDROXIDE, silica-free. Bubble ammonia gas into distilled water contained in a plastic bottle until the solution is saturated (Note 2).

SULPHURIC ACID, 8, 40 and 50% *V/V*. Store the solutions in plastic bottles.

HYDROFLUORIC ACID, 25% *V/V*. Store the solution in a plastic bottle (Note 3).

N-AMYL ALCOHOL. Reagent-grade.

CALIBRATION CURVE

Add 4 mL of 8% sulphuric acid to each of six 100-mL plastic or teflon beakers (Note 4); then by burette, add to the last five beakers 1,

2.5, 5, 7.5 and 10 mL, respectively, of the dilute standard 10-µg/mL silicon solution. The contents of the first beaker constitute the blank. Add 20 mL of 5% boric acid solution and 5 mL of 8% ammonium molybdate solution to each beaker and dilute the solutions to about 40 mL with water. Using a pH meter, adjust the pH of each solution to 2.0 ± 0.2 with silica-free ammonium hydroxide and dilute the solutions to about 50 mL with water. Cover the beakers with teflon covers, heat the solutions in a hot water-bath maintained at about 100°C for 30 min, then cool them to about room temperature in a water-bath. Transfer the resulting solutions to 100-mL volumetric flasks, dilute them to volume with water, mix them thoroughly and immediately transfer them back to the original plastic or teflon beakers (Note 5).

Transfer a 20-mL aliquot of each solution to a 60-mL separatory funnel containing 5 mL of 40% sulphuric acid and immediately mix the solution thoroughly (Note 6). By pipette, add 10 mL of n-amyl alcohol to each funnel, then close the funnel and shake it for 2 min. Allow about 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Wash each extract by shaking it for about 1 min with 10 mL of 8% sulphuric acid (Note 7), allow the layers to separate and drain off and discard the aqueous layer. Drain the resulting n-amyl alcohol extracts into dry 15-mL centrifuge tubes and centrifuge them for 1 min. Measure the absorbance of each extract (Note 8) at 350 nm (Note 9) against n-amyl alcohol as the reference solution, using 20-mm cells (Note 10). Correct the absorbance value obtained for each α-silicomolybdic acid extract by subtracting that obtained for the blank extract. Plot micrograms of silicon vs absorbance.

PROCEDURE

In this procedure a reagent blank is carried along with the samples (Note 11).

Transfer 0.5-1 g of sample to a 100-mL plastic or teflon beaker (Note 4), add 5 mL of water and 4 mL of 50% sulphuric acid, then cover the beaker with a teflon cover and add 2 mL of concentrated nitric acid. Place the beaker in a hot water-bath and heat the solution gently for about 1 h to dissolve the sample and to remove oxides of nitrogen. Cool the solution to room temperature, add 2 mL of 25% hydrofluoric acid (Note 12) and heat the solution in a hot water-bath maintained at 60-70°C for 30 min (Note 13). Add 20 mL of 5% boric acid solution, allow the solution to stand for about 15 min to ensure the complete complexation of the excess hydrofluoric acid, then add 5 mL of 8% ammonium molybdate solution. Neutralize part of the excess acid by adding 2 or 3 mL of silica-free ammonium hydroxide (Note 14), then proceed with the pH adjustment, the formation of α-silicomolybdic acid and the subsequent dilution of the solution to 100 mL with water.

Transfer suitable identical 10-20-mL aliquots of the resulting sample and blank solutions to 60-mL separatory funnels containing 5 mL of 40% sulphuric acid. If necessary, dilute the solutions to approximately 25 mL with water and proceed with the extraction of the α-silicomolybdic acid complex and the subsequent measurement of the absorbance as described above. Correct the absorbance value obtained for the reagent blank extract and determine the silicon content of the aliquot by reference to the calibration curve.

NOTES

1. Plastic or teflon beakers used for the dissolution of the melt, and plastic bottles used for the storage of solutions should be cleaned with dilute hydrofluoric acid and then washed with water to prevent contamination from silica. Glassware can be cleaned with 25% ammonium hydroxide and then washed with concentrated hydrochloric acid and with water.
2. The concentration of the solution can be tested by titrating a 5-mL aliquot with concentrated hydrochloric acid - using phenolphthalein as indicator - and comparing the result obtained with that obtained for the titration of the same volume of concentrated ammonium hydroxide.
3. Hydrofluoric acid with a low fluosilicic acid content should be used.

4. Plastic beakers previously used 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, a low result will be obtained for silicon, particularly for samples containing phosphorus, because of the "seeding effect" described by Morrison and Wilson (3), which results in the precipitation of part of the phosphomolybdic acid.
5. This transfer is necessary so that the solution will not remain in contact with glass.
6. The α-silicomolybdic acid complex decomposes slightly when the solution is allowed to stand for more than about 2 h. Consequently, the complex should be extracted within about 2 h after complex formation.
7. Washing the extract with about 1.5 M sulphuric acid partly removes coextracted molybdic acid which absorbs at the wavelength used for measuring the absorbance of the silicon complex.
8. The absorbance of the n-amyl alcohol extract of the α-silicomolybdic acid complex remains constant for at least 3 h. The apparent molar absorptivity of the complex in n-amyl alcohol at 350 nm (Note 9), based on complete extraction of silicon and a 10-mL volume, is 7.98×10^2 $L.mol^{-1}.mm^{-1}$.
9. Although the wavelength of maximum absorption of α-silicomolybdic acid occurs at approximately 307 nm, wavelengths below 350 nm are not recommended for spectrophotometric measurement because of the magnitude of the reagent blank.
10. The extracts contain 2, 5, 10, 15 and 20 μg of silicon, respectively. The calibration curve can be extended to 40 μg of silicon if 10-mm cells are used.
11. It is recommended that two reagent blanks should be carried along with the samples because of the ease with which solutions may become contaminated by silicon-bearing dust in the air.
12. Hydrofluoric acid is added to ensure the decomposition of refractory silicides and to convert colloidal or polymerized silicic acid to the monomeric or "reactive" form.
13. Silica may be lost by volatilization as the fluoride if the solution is heated at a higher temperature.
14. This reduces the time in which the solution is in contact with the glass electrode.

ACCURACY

Illustrated in Tables 18 and 19 in Appendix A.

OTHER APPLICATIONS

This method can probably be used to determine silicon in nickel-, zinc- and cobalt-base alloys.

REFERENCES

1. Donaldson, E.M. and Inman, W.R. "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)"; Mineral Sciences Division Bulletin TB 77; Mines Branch, Energy, Mines and Resources Canada; 1965.

2. Wadelin, C. and Mellon, M.G. "Extraction of heteropoly acids - Application to determination of phosphorus"; Anal Chem 25:1668-1673; 1953.

3. Morrison, I.R. and Wilson, A.L. "The absorptiometric determination of silicon in water. Part I. Formation, stability and reduction of α- and β-molybdosilicic acids"; Analyst 88: 88-99; 1963.

SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM IN COPPER METAL AND ALLOYS BY CHLOROFORM EXTRACTION OF THE TELLURIUM (IV) HEXABROMIDE-DIANTIPYRYLMETHANE COMPLEX AFTER SEPARATION BY IRON COLLECTION AND XANTHATE EXTRACTION

PRINCIPLE

Tellurium is separated from matrix elements by coprecipitating tellurium (VI) with hydrous ferric oxide from an ammoniacal medium. The precipitate is dissolved in 12 M hydrochloric acid and tellurium is reduced to tellurium (IV) with chloride ion by heating the solution. It is subsequently separated from iron by chloroform extraction of its ethyl xanthate complex. Tellurium is ultimately determined spectrophotometrically by measuring the absorbance at 336 nm of the yellow 1:6:2 tellurium (IV) hexabromide-diantipyrylmethane ion-association complex, after extraction of the complex into chloroform from a 2 M sulphuric acid-0.6 M potassium bromide medium. The molar absorptivity of the complex in chloroform at this wavelength is 1.82×10^3 $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCES

Platinum (IV), palladium (II), gold (III), rhenium (VII), selenium (IV) and arsenic (III) are also extracted as xanthates, either completely or to a large extent, from about 10 M or more concentrated hydrochloric acid media (2). Iron (III), copper (II) and molybdenum (VI) are extracted to a slight extent from 12 M hydrochloric acid (1) and germanium is extracted as the chloro-complex (2). Platinum, palladium, gold, rhenium, germanium and molybdenum are not usually present in copper-base alloys. However, platinum, palladium, gold and molybdenum would be separated from tellurium to a large extent by the coprecipitation step. Up to at least 500 µg each of selenium (IV), rhenium (VII) and germanium, up to 50 µg of platinum (IV) and 25 µg of palladium (II), and up to 5 mg each of arsenic (III), arsenic (V) and iron (III) do not interfere during complex formation (1). The amount of copper retained in the hydrous oxide precipitate after a single coprecipitation step inhibits or completely prevents the extraction of tellurium as the xanthate. However, interference from residual copper is avoided by removing most of it by a second precipitation step. The remaining copper, which is coextracted to a slight extent with tellurium xanthate, does not cause error in the tellurium result (1).

Antimony (V), tin (IV) and bismuth are also coprecipitated with hydrous ferric oxide from an ammoniacal medium. Tin and bismuth do not interfere but more than 1 mg of antimony (V) causes a high result for tellurium because it is partly coextracted as the chloro-complex during the xanthate extraction step and it subsequently forms a similar extractable bromide-diantipyrylmethane complex. Interference from up to at least 50 mg of antimony is eliminated by washing the extract with water (1).

Large amounts of sulphate salts that are retained in the hydrous oxide precipitate after a single coprecipitation step may interfere in the subsequent reduction of tellurium in a concentrated hydrochloric acid medium. Nitrate salts interfere in a similar manner (1).

RANGE

This method is suitable for samples containing 0.0001 to 0.2% of tellurium.

REAGENTS

STANDARD TELLURIUM SOLUTION, 0.2 mg/mL. Dissolve 0.1251 g of pure tellurium dioxide by heating it gently with 25 mL of concentrated nitric acid, then cool the solution and dilute it to 500 mL with water. Prepare a 10-µg/mL solution by diluting 10 mL of this stock solution to 200 mL with water. Prepare the diluted solution fresh as required.

DIANTIPYRYLMETHANE SOLUTION, 4% *m/V* in ethyl alcohol. Prepare a fresh solution every seven days (Note 1).

IRON (III) SULPHATE SOLUTION, 20 mg of iron/mL. Dissolve 25 g of ferric sulphate monohydrate in hot water, add 10 mL of 50% sulphuric acid, then cool the solution and dilute it to 250 mL with water.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

POTASSIUM BROMIDE SOLUTION, 3 M.

POTASSIUM SULPHATE SOLUTION, 2.5% *m/V*.

SULPHURIC ACID, 10 M and 50% *V/V*.

NITRIC ACID, 50% *V/V*.

HYDROCHLORIC ACID, 20% *V/V*.

AMMONIUM HYDROXIDE, 5% *V/V*.

CHLOROFORM. Reagent-grade and chromatoquality-reagent (alcohol- and peroxide-free).

CALIBRATION CURVE

Add 2 mL of 2.5% potassium sulphate solution and 2 or 3 drops of 50% sulphuric acid to each of eight 50-mL beakers; then by burette, add to the last seven beakers 0.5, 1, 2, 3, 4, 5 and 6 mL, respectively, of the dilute standard 10-µg/mL tellurium solution. The contents of the first beaker constitute the blank. Evaporate each solution to dryness or to near dryness, then wash down the sides of the beakers with a small amount of water and evaporate the solutions to dryness again to ensure the complete removal of nitric acid. Add 5 mL of 10 M sulphuric acid and 2 or 3 mL of water to each beaker, heat the solutions gently for 2 or 3 min, then cool then to room temperature in a water-bath.

Transfer the resulting solutions to 60-mL separatory funnels marked at approximately 25 mL and containing 5 mL of 3 M potassium bromide solution. Add 2 mL of 4% diantipyrylmethane solution to each funnel, then dilute the solutions to the mark with water, mix them thoroughly and allow them to stand for 15 min to complete the complex formation. By pipette, add 10 mL of chromatoquality chloroform to each funnel, then close it and shake it for 2 min. Allow several minutes for the layers to separate, then drain the resulting chloroform layers into dry 15-mL centrifuge tubes and centrifuge them for 1 min (Note 2). Measure the absorbance of each extract (Note 3) at 336 nm against chloroform as the reference solution, using 10-mm cells. Correct the absorbance value obtained for each tellurium bromide-diantipyrylmethane extract by subtracting that obtained for the blank extract. Plot micrograms of tellurium vs absorbance.

PROCEDURE

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

Transfer 0.5-1 g of sample containing up to about 1 mg of tellurium to a 400-mL beaker, then cover the beaker and add 20 mL of 50% nitric acid. When the sample has dissolved, add 25 mL of 50% sulphuric acid and heat the solution until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, add about 100 mL of water, 5 mL of concentrated hydrochloric acid and 4 mL of iron (III) sulphate solution. Cover the beaker and heat the solution to dissolve the salts.

Add sufficient concentrated ammonium hydroxide to the resulting solution to precipitate iron as the hydrous oxide, then add 5 mL in excess and boil the solution to coagulate the precipitate. Allow it to settle, then using Whatman No. 40 paper, filter the hot solution and transfer the bulk of any insoluble material to the filter paper with a jet of 5% ammonium hydroxide. Wash the paper and the precipitate twice with 5% ammonium hydroxide, then discard the filtrate. Place the original beaker under the funnel and dissolve the precipitate with hot 20% hydrochloric acid. Wash the paper 3 times with the hot acid solu-

tion, then discard it. Wash down the sides of the beaker with the hot acid solution, then reprecipitate the iron and filter the solution as described above. Wash the beaker twice and wash the paper and the precipitate 3 times with 5% ammonium hydroxide. Place a 125-mL Erlenmeyer flask under the funnel, then wash the beaker that contained the precipitate 3 times with concentrated hydrochloric acid added from a plastic wash bottle. Add the washings to the paper containing the precipitate. When the precipitate has dissolved, wash the paper 3 times with concentrated hydrochloric acid (Note 4), then discard it.

Heat the resulting solution at 90-95°C in a hot water-bath for 30 min to ensure the complete reduction of tellurium (VI) to tellurium (IV), then cool it to room temperature in a water-bath. Transfer the solution to a 125-mL separatory funnel, using concentrated hydrochloric acid to wash the flask and, if necessary, dilute it to approximately 50 mL with concentrated hydrochloric acid. Add 10 mL of reagent-grade chloroform, then add 1 mL of freshly prepared 20% potassium ethyl xanthate solution (Note 5), close the funnel and extract the solution immediately (Note 6) by shaking the funnel for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-mL separatory funnel. Extract the aqueous phase two more times in a similar manner with 10- and 5-mL portions of chloroform and 1 and 0.5 mL of xanthate solution, respectively, then wash it by shaking it for about 30 s with 5 mL of chloroform. Add 15 mL of water and 0.2 mL of xanthate solution to the combined extracts, then close the funnel and shake it for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 150-mL beaker. Wash the aqueous phase 3 times by shaking it for about 30 s each time with 3 mL of chloroform and add the washings to the beaker containing the initial extract. Add 10 mL of 50% nitric acid to the resulting extract and heat the mixture in a hot water-bath to remove the chloroform. Add 0.5 mL of 50% sulphuric acid and 2 mL of 2.5% potassium sulphate solution, then cover the beaker and heat the solution until the volume has been reduced to approximately 3 mL. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to dryness or to near dryness.

If the sample contains 60 µg or less of tellurium, evaporate the resulting sample and blank solutions to dryness or to near dryness again - after washing down the sides of the beakers with a small amount of water - to ensure the complete removal of nitric acid (Note 7). Cool the beakers and add 5 mL of 10 M sulphuric acid and 2 or 3 mL of water. Heat the solutions gently for 2 or 3 min, then cool them to room temperature and proceed with the formation and the extraction of the tellurium (IV) bromide-diantipyrylmethane complex (Note 8) 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 reagent blank extract and determine the tellurium content of the sample extract by reference to the calibration curve.

If the sample contains more than 60 µg of tellurium, add 10 mL of 50% nitric acid to the sample and blank solutions and heat them gently to dissolve the salts. Cool the solutions, transfer them to volumetric flasks of appropriate size - 50-200 mL - and dilute them to volume with water. Transfer a suitable identical 10-50-mL aliquot of each solution to 150-mL beakers, add 2 or 3 drops of 50% sulphuric acid and 2 mL of 2.5% potassium sulphate solution and proceed with the removal of nitric acid by evaporation (Note 7), the complex formation and the subsequent determination of the tellurium content of the aliquot as described above.

NOTES

1. Pure white diantipyrylmethane is recommended. The yellow compound sold by some manufacturers yields a high blank.
2. Filtration of the extracts through cotton-wool or filter paper to remove water droplets is not recommended because of possible contamination from residual organic and other materials that absorb in the near ultraviolet.
3. The absorbance of the chloroform extract of the tellurium hexabromide-diantipyrylmethane

complex remains constant for at least 2 h.

4. It is not necessary to remove all the yellow colour caused by iron from the filter paper. The total volume of the sample solution should be 40-50 mL at this stage.
5. The xanthate solution should be added by pipette using a suction bulb or by using a graduated or marked medicine dropper and the extraction should be carried out in a fume hood. Prolonged exposure to xanthate vapour can produce an allergic reaction.
6. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.
7. If organic material, indicated by a dark-brown or yellow colour, is present after the solution has been evaporated to dryness, add 5 mL of 10 M sulphuric acid and 3 mL of concentrated nitric acid, then cover the beaker and heat the solution to destroy the organic material. Remove the cover and evaporate the solution to fumes of sulphur trioxide twice after washing down the sides of the beaker with water each time. Cool the solution, add approximately 3 mL of water and proceed as described.
8. The presence of a small amount of coextracted copper is indicated by the reddish colour obtained when the sample solution is added to the potassium bromide solution in the separatory funnel. This colour disappears when the resulting solution is diluted with water.

ACCURACY

Illustrated in Table 20 in Appendix A.

REFERENCES

1. Donaldson, E.M. "Spectrophotometric determination of tellurium in concentrates and brasses by chloroform extraction of the tellurium (IV) hexabromide-diantipyrylmethane complex after separations by iron collection and xanthate extraction"; Talanta 23:823-827; 1976.

2. Idem. "Chloroform extraction of metal ethyl xanthates from hydrochloric acid media"; ibid 23:411-416; 1976.

ATOMIC-ABSORPTION DETERMINATION OF TIN IN IRON, STEEL AND COPPER-, ZIRCONIUM-, TITANIUM-, ALUMINUM- AND ZINC-BASE ALLOYS AFTER SEPARATION BY EXTRACTION AS THE IODIDE

PRINCIPLE

Tin is separated from matrix elements by toluene extraction of tin iodide from a 3 M sulphuric acid-1.5 M potassium iodide medium containing tartaric and ascorbic acids. It is subsequently back-extracted into a nitric-hydrochloric-sulphuric acid solution and ultimately determined by atomic-absorption spectrophotometry at 235.4 nm in a strongly reducing nitrous oxide-acetylene flame in a 10% hydrochloric acid-0.5% tartaric acid medium containing 250 µg/mL of potassium as the chloride (1).

INTERFERENCES

Only arsenic is significantly coextracted as the iodide under the conditions used for the extraction of tin (2,3) but up to 20 mg does not interfere in the extraction or in the subsequent determination of tin in a nitrous oxide-acetylene flame when the final solution is diluted to 10 mL or more. However, arsenic will interfere in the back-extraction of tin into solutions containing nitric acid unless hydrochloric acid is present. This is because arsenic and tin react to form a compound that is insoluble in nitric acid (1). The coextraction of antimony and germanium is minimal from 1.5 M potassium iodide and from 3 M sulphuric acid media, respectively (2), and thallium forms an insoluble yellow iodide that remains to a large extent in the toluene phase. Up to 50 mg of antimony does not interfere (1). Germanium and thallium are not usually present in ferrous and non-ferrous alloys.

Lead precipitates as the sulphate and tungsten forms an insoluble compound in the sulphuric acid medium used for the extraction of tin. However, a large amount of lead and up to about 10 mg of tungsten do not interfere if the precipitates are removed by filtration before the extraction step. More than about 100 mg of copper may interfere with the extraction of tin by precipitating as cuprous iodide. The reduction of iron (III) with potassium iodide, which results in the presence of a large amount of iodine in the toluene phase, is prevented by reducing it with ascorbic acid before the addition of iodide (1).

Potassium iodide that is retained in the toluene phase causes a high result for tin because potassium suppresses its ionization in the flame (4,5). This interference is eliminated by washing the extract with 9 M sulphuric acid-0.05 M potassium iodide solution to reduce the amount of entrained potassium iodide, and by adding approximately 250 µg/mL of potassium as the chloride to the sample and calibration solutions (1).

RANGE

This method is suitable for iron, steel and aluminum-, zinc- and zirconium-base alloys containing approximately 0.001 to 5% of tin. It is suitable for titanium- and copper-base alloys containing approximately 0.005 to 5% of tin.

REAGENTS

STANDARD TIN SOLUTION, 1000 µg/mL. Dissolve 0.5000 g of pure tin metal by heating it gently in a covered 400-mL beaker with 50 mL of concentrated sulphuric acid and 5 mL of 30% hydrogen peroxide, then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool the solution in a water-bath and carefully add about 25 mL of water. Transfer the solution to a 500-mL volumetric flask containing 150 mL of 50% sulphuric acid, dilute it almost to the mark with water and mix it gently by swirling the flask. Cool the resulting solution to room temperature and dilute it to volume with water.

POTASSIUM-TARTARIC ACID SOLUTION, 2500 µg/mL and 5% *m/V*, respectively. Dissolve 4.77 g of potas-

sium chloride and 50 g of tartaric acid in about 500 mL of water and dilute the solution to 1 L. If necessary, filter the resulting solution.

POTASSIUM IODIDE SOLUTION, 5.3 M (88% *m/v*). Prepare a sufficient volume of solution just before use.

SULPHURIC ACID, 3 M. Dilute 65 mL of 50% sulphuric acid to 200 mL with water. Store the solution in a plastic wash-bottle.

SULPHURIC ACID-POTASSIUM IODIDE SOLUTION, 9 M and 0.05 M, respectively. Add 0.5 mL of 5.3 M potassium iodide solution to 50 mL of 50% sulphuric acid. Prepare the solution immediately before use (Note 1).

SULPHURIC ACID-NITRIC ACID SOLUTION, 10% and 50% *V/V*, respectively.

TARTARIC ACID SOLUTION, 20% *m/V*.

SULPHURIC ACID, 5 and 50% *V/V*.

TOLUENE. Reagent-grade.

CALIBRATION SOLUTIONS

Add 10 mL of 10% sulphuric acid-50% nitric acid solution, 2 mL of concentrated hydrochloric acid and 5 drops of concentrated perchloric acid to each of eleven 100-mL beakers; then by burette, add to the first ten beakers, 0.2, 0.5, 1, 1.5, 2, 2.5, 3, 4, 5 and 6 mL, respectively, of the standard 1000-μg/mL tin solution. The contents of the last beaker constitute the zero calibration solution. Cover each beaker, evaporate the solutions to fumes of perchloric acid or sulphur trioxide, then remove the covers and evaporate the solutions to dryness. Cool the solutions, wash down the sides of the beakers with water and evaporate the solutions to dryness again to ensure the complete removal of sulphuric acid. Add 10 mL each of concentrated hydrochloric acid and 2500-μg/mL potassium-5% tartaric acid solution to each beaker and mix the solutions to dissolve the salts. Cool the solutions, transfer them to 100-mL volumetric flasks and dilute them to volume with water (Note 2).

PROCEDURES

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

A - Iron, steel and aluminum- and zinc-base alloys

Transfer 0.1-1 g of sample (Note 3) containing up to about 5 mg of tin and not more than about 10 mg of tungsten to a 400-mL teflon beaker. Cover the beaker and add 25 mL of water and 10 mL of concentrated nitric acid. Heat the mixture gently until the sample is decomposed, then add 55 mL of 50% sulphuric acid and heat the solution until the evolution of oxides of nitrogen ceases. Remove the cover, add 1 mL of concentrated hydrofluoric acid and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, wash down the sides of the beaker with water and evaporate the solution to fumes of sulphur trioxide again to ensure the complete removal of hydrofluoric acid (Note 4). Cool the solution to room temperature, then cover the beaker and add 5 mL of 20% tartaric acid solution and 50 mL of water. Heat the solution to dissolve the salts, then cool it to room temperature and, if necessary, filter it - using Whatman No. 541 paper - into a 400-mL beaker. Wash the beaker 3 times with small portions of water. Wash the paper once with 5% sulphuric acid added from a plastic wash-bottle, then wash it with water. Discard the paper. Evaporate the filtrate to about 85 mL and cool it to room temperature.

Add 1 g of ascorbic acid (Note 5) to the resulting solution and mix it thoroughly. Transfer the solution to a 250-mL separatory funnel marked at 100 mL and dilute it to the mark with water. Add 40 mL of freshly prepared 5.3 M potassium iodide solution and 30 mL of toluene, close the funnel and shake it for 2 min. Allow several minutes for the layers to separate, then drain the lower aqueous layer into a second 250-mL separatory funnel. Wash the stem of the first funnel with 3 M sulphuric acid and collect the washings in the second funnel. Add about 1 mL of 5.3 M potassium iodide solution to the first funnel con-

taining the extract and, without mixing, drain the resulting aqueous layer into the second funnel (Note 6). Wash the stem of the first funnel again with 3 M sulphuric acid. Add 20 mL of toluene to the second funnel and extract the solution again by shaking it for 2 min. Allow the layers to separate, then drain off and discard the aqueous phase. Add the second extract to the first extract and, while the stem of the second funnel is in the neck of the first funnel, wash down the sides of the funnel with toluene added from a plastic wash-bottle. Drain off and discard the residual aqueous phase remaining in the first funnel, then add 10 mL of freshly prepared 9 M sulphuric acid-0.05 M potassium iodide solution (Note 1) and, without delay, shake the funnel gently for about 30 s. Allow the layers to separate, then drain off and discard the aqueous layer. Repeat the washing step with 10 mL of a second freshly prepared wash solution. Drain off the aqueous layer and wash the stem of the funnel with water to remove the residual wash solution.

Add 10 mL of 10% sulphuric acid-5% nitric acid solution and 2 mL of concentrated hydrochloric acid to the combined extracts, close the funnel and shake it for 1 min. Allow the layers to separate, then drain the aqueous layer into a 100-mL beaker and wash the stem of the funnel with water. Wash the toluene phase twice by shaking it for about 30 s each time with 5-mL portions of water and add the washings to the beaker (Note 7). Add 5 drops of concentrated perchloric acid to the resulting solution, cover the beaker and evaporate the solution to fumes of perchloric acid or sulphur trioxide, then remove the cover and evaporate the solution to dryness. Cool the beaker, wash down the sides with water and evaporate the solution to dryness again to ensure the complete removal of sulphuric acid.

Add 1 mL each of concentrated hydrochloric acid and 2500-μg/mL potassium-5% tartaric acid solution to the beaker containing the blank. Depending on the expected tin content, add sufficient concentrated hydrochloric acid and potassium-tartaric acid solution to the beaker containing the sample so that 1 mL of each will be present for each 10 mL of final solution. Heat the resulting solutions for about 5 min in a hot water-bath (Note 8), then cool them to room temperature. Transfer the blank solution to a 10-mL volumetric flask and transfer the sample solution to a flask of appropriate size - 10-100 mL. Dilute each solution to volume with water.

Measure the absorbance of the resulting solutions at 235.4 nm in a strongly reducing nitrous oxide-acetylene flame (Note 9). Determine the tin contents, in milligrams, of the solutions by relating the resulting values to those obtained concurrently for calibration solutions of slightly higher and lower tin concentrations. Correct the result obtained for the sample solution by subtracting that obtained for the reagent blank solution.

B - Zirconium-base alloys

Transfer up to 1 g of sample to a 400-mL teflon beaker. Cover the beaker and add 55 mL of 50% sulphuric acid and 1 mL of concentrated hydrofluoric acid. Heat the mixture gently until the sample is decomposed, then remove the cover and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, wash down the sides of the beaker with water and evaporate the solution to fumes of sulphur trioxide again to ensure the complete removal of hydrofluoric acid (Note 4). Cool the solution, add 5 mL of 20% tartaric acid solution and 50 mL of water and proceed with the extraction (Note 10) and the subsequent determination of tin as described in Procedure A.

C - Titanium-base alloys

Transfer up to 0.25 g of sample (Note 11) to a 400-mL beaker, cover the beaker and add 55 mL of 50% sulphuric acid. Heat the mixture until the sample is decomposed, then remove the cover, evaporate the solution to fumes of sulphur trioxide and proceed as described in Procedure B (Note 10).

D - Copper-base alloys

Decompose up to 0.2 g of sample containing not more than about 100 mg of copper and determine tin by the method described in Procedure A (Note 12).

NOTES

1. This solution must be prepared and used immediately because potassium iodide is rapidly oxidized by air to iodine in strongly acidic solutions.
2. The calibration solutions are stable for at least one week.
3. This decomposition procedure is not suitable for samples of high chromium content - i.e., stainless steel. However, up to 0.5 g of sample can readily be dissolved by treating it with 55 mL of 50% sulphuric acid and 20 mL of aqua regia. After removing the oxides of nitrogen by boiling, proceed as described. The use of more than 0.5 g of sample is not recommended because the chromium (III) sulphate salts that are formed may not dissolve completely when the solution is ultimately diluted with water and heated.
4. Tin will not be quantitatively extracted as the iodide if hydrofluoric acid is not completely removed, and if too much sulphuric acid is removed by evaporation.
5. Because of their high iron content, add 2 g of ascorbic acid for samples of iron or steel.
6. By this procedure, the aqueous phase that remains in the bore of the stop-cock is transferred to the second funnel.
7. The toluene can be used for subsequent extractions if the toluene phases are combined in a large separatory funnel and washed twice by shaking with about 3% sodium hydroxide solution and then washed 3 times by shaking with 10% sulphuric acid.
8. If the sample contains arsenic, heating is necessary to ensure the complete dissolution of the tin-arsenic compound that is formed when the sample solution is evaporated to dryness in the presence of nitric and sulphuric acids. This compound is only sparingly soluble in cold hydrochloric acid.
9. A strongly reducing, non-luminous nitrous oxide-acetylene flame is required to obtain the highest sensitivity for tin. The height at which the beam from the hollow-cathode lamp passes through the flame is also extremely important (6). Consequently, after all other instrumental parameters have been set, the acetylene and nitrous oxide flow-rates should be adjusted to give the maximum "red feather" - 15-20 mm - without producing a luminous flame. Under these conditions, very little carbon is deposited in the burner slot. Subsequently, the height of the burner should be adjusted to give maximum absorbance while a solution containing tin is aspirated into the flame. About two- to five-fold scale expansion is recommended for the determination of tin. Because of the moderately high "noise" level of the analytical signal, a 10-s integration time is also recommended to improve the precision of the determination.
10. The addition of ascorbic acid before the extraction step is not necessary if the sample contains very little iron.
11. The use of more than about 0.25 g of sample is not recommended because a precipitate forms during the extraction step.
12. If silicon is absent, use a pyrex beaker and omit the addition of hydrofluoric acid.

ACCURACY

Illustrated in Table 21 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine tin in nickel-base alloys.

REFERENCES

1. Donaldson, E.M. "Determination of tin in ores, iron, steel and alloys by atomic-absorption spectrophotometry after separation by extraction as the iodide"; Talanta 27:499-505; 1980.

2. Byrne, A.R. and Gorenc, D. "The toluene extraction of some elements as iodides from sulfuric acid-potassium iodide media. Application to neutron activation analysis - Part I: Extraction behaviour of As, Au, Bi, Br, Cd, Cu, Ga, Ge, In, Hg, Mo, Pb, Sb, Se, Sn, W and Zn"; Anal Chim Acta 59:81-89; 1972.

3. Donaldson, E.M. "Determination of tin in ores, steel and alloys with gallein after extraction as the iodide"; Mineral Sciences Division Bulletin TB 195; Mines Branch, Energy, Mines and Resources Canada; 1974.

4. Juliano, P.O. and Harrison, W.W. "Atomic absorption interferences of tin"; Anal Chem 42:84-89; 1970.

5. Levine, J.R., Moore, S.G. and Levine, S.L. "Effect of potassium on determination of tin by atomic absorption spectrophotometry"; ibid 42:412-414; 1970.

6. Capacho-Delgado, L. and Manning, D.C. "Determination of tin by atomic absorption spectroscopy"; Spectrochim Acta 22:1505-1513; 1966.

SPECTROPHOTOMETRIC DETERMINATION OF TIN IN IRON, STEEL AND COPPER-, ZIRCONIUM-, ALUMINUM- AND ZINC-BASE ALLOYS WITH GALLEIN AFTER SEPARATION BY EXTRACTION AS THE IODIDE

PRINCIPLE

Tin is separated from matrix elements by toluene extraction of tin iodide from a 2 M sulphuric acid-1.5 M potassium iodide medium containing tartaric and ascorbic acids. It is subsequently back-extracted into dilute sodium hydroxide solution. Tin is ultimately determined spectrophotometrically by measuring the absorbance at 496 nm of the red tin (IV)-gallein complex, after extraction of the complex into n-amyl alcohol at pH 2.25 from a monochloroacetic acid-ascorbic acid medium. The molar absorptivity of the complex in n-amyl alcohol at this wavelength is 4.11×10^3 $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCES

The extraction procedure (2) eliminates interference from elements that oxidize gallein - i.e., iron (III), manganese (VII), vanadium (V), chromium (VI) and cerium (IV) (3) - and from most of the elements that form coloured complexes with gallein - i.e., bismuth, thorium, aluminum, gallium, molybdenum (VI), tungsten (VI), copper (II), zinc, tellurium (IV) and titanium (IV) (3-6). Antimony (III) and germanium are partly coextracted as iodides and, if moderate amounts are present, they will interfere during complex formation. Germanium, cerium, thorium and gallium are not usually present in ferrous and non-ferrous alloys. Up to 3 mg of antimony and up to 2 mg of germanium can be present in the aliquot taken for extraction without producing significant error in the tin result. Up to at least 50 mg of iron (III), aluminum, zinc and zirconium, and up to at least 10 mg of cobalt (II), nickel, cadmium, manganese (II), chromium (VI), titanium (IV), vanadium (V), molybdenum (VI), mercury (II), gallium, indium, bismuth, arsenic (III), arsenic (V) and tellurium (IV) do not interfere (1). More than about 100 mg of copper may interfere with the extraction of tin by precipitating as cuprous iodide (7).

More than 1 mg of thallium (I) interferes in the extraction of tin because it forms a yellow iodide precipitate that remains to a large extent in the toluene phase. Lead precipitates as the sulphate and tungsten forms an insoluble hydrolysis compound in the sulphuric acid medium used for the extraction of tin. However, a large amount of lead and up to about 10 mg of tungsten do not interfere if the precipitates are removed by filtration before the extraction step (7). Selenium may be coextracted during the separation of tin as the iodide (2) and may interfere during complex formation (3,4). The reduction of iron (III) with potassium iodide, which results in the presence of a large amount of iodine in the toluene phase, is prevented by reducing it with ascorbic acid before the addition of iodide (7). Interference from coextracted iodine is eliminated by reducing it with ascorbic acid before the formation of the tin complex.

NOTE: The atomic-absorption iodide extraction method (p 83) is recommended for samples containing 1% or more of tin.

RANGE

This method is suitable for samples containing approximately 0.0005 to 1% of tin but material containing higher concentrations can also be analyzed with reasonable accuracy.

REAGENTS

STANDARD TIN SOLUTION, 1 mg/mL. Prepare the solution as described in the atomic-absorption-iodide extraction method for tin (p 83). Dilute 20 mL of this stock solution to 100 mL with 25% sulphuric acid. Prepare a 5-µg/mL solution by diluting 5 mL of the resulting solution and 20 mL of

concentrated hydrochloric acid to 200 mL with water. Prepare the diluted solution fresh as required.

GALLEIN (4,5-dihydroxyfluorescein) SOLUTION, 0.06% *m/V* in ethyl alcohol. This solution is stable for at least one month.

MONOCHLOROACETIC ACID SOLUTION, 40% *m/V*.

ASCORBIC ACID SOLUTION, 5% *m/V*. Prepare a fresh solution every five days.

HYDROCHLORIC ACID, 10% *V/V*.

SULPHURIC ACID, 2.8 M. Add 310 mL of concentrated sulphuric acid - slowly and while stirring the solution - to about 1600 mL of water in a 2-L beaker. Allow the solution to cool to room temperature, then transfer it to a 2-L volumetric flask and dilute it to volume with water.

SULPHURIC ACID, 5 and 50% *V/V*.

TARTARIC ACID SOLUTION, 25% *m/V*.

POTASSIUM IODIDE SOLUTION, 5.3 M (88% *m/V*). Prepare a sufficient volume of solution just before use.

POTASSIUM IODIDE-SULPHURIC ACID SOLUTION, 1.5 M and 2 M, respectively. Add 40 mL of 5.3 M potassium iodide solution to 100 mL of 2.8 M sulphuric acid. Prepare the solution fresh just before use.

SODIUM HYDROXIDE SOLUTION, 2% *m/V*. Store the solution in a plastic bottle.

N-AMYL ALCOHOL. Reagent-grade.

TOLUENE. Reagent-grade.

CALIBRATION CURVE

To six 100-mL beakers, add by burette, 1, 2, 3, 4, 5 and 6 mL, respectively, of the dilute standard 5-µg/mL tin solution and dilute each solution to 20 ± 0.5 mL with 10% hydrochloric acid. Add 20 mL of 10% hydrochloric acid to a seventh beaker; this constitutes the blank. In succession, add 5 mL of 40% monochloroacetic acid solution, 2 mL of 5% ascorbic acid solution and 2 mL of concentrated ammonium hydroxide to each beaker, mix the solutions thoroughly, then cool them to room temperature in a water-bath. Using a pH meter, adjust the pH of each solution to 2.25 ± 0.01 (Note 1) with concentrated ammonium hydroxide and with 10% hydrochloric acid if required.

Transfer the resulting solutions to 60-mL separatory funnels marked at approximately 50 mL and dilute them to the mark with water (Note 2). Add exactly 1 mL of 0.06% gallein solution, mix the solutions thoroughly, then allow them to stand for 15 min to complete the complex formation. By pipette, add 10 mL of n-amyl alcohol to each funnel, then close it and shake it for 2 min. Allow several minutes for the layers to separate, then drain off and discard the lower aqueous layers. Drain the resulting n-amyl alcohol extracts into dry 15-mL centrifuge tubes and centrifuge them for 1 min. Measure the absorbance of each tin-gallein extract (Note 3) at 496 nm against the blank extract as the reference solution, using 10-mm cells. Plot micrograms of tin vs absorbance.

PROCEDURE

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

Decompose 0.5 g of sample as described in the appropriate atomic-absorption method for tin (p 84) using 80 mL of 50% sulphuric acid instead of 55 mL (Notes 4 and 5). After evaporating the solution to fumes of sulphur trioxide twice to remove hydrofluoric acid, cool the solution to room temperature and add 10 mL of 25% tartaric acid solution and about 100 mL of water. If necessary, heat the solution gently to dissolve the salts, then cool it to room temperature and, if necessary, filter it - using Whatman No. 541 paper - into a 250-mL volumetric flask. Wash the beaker 3 times with small portions of water. Wash the paper once with 5% sulphuric acid added from

a plastic wash-bottle, then wash it with water. Discard the paper. Dilute the filtrate to volume with water (Notes 6 and 7).

Transfer a 20-50-mL aliquot of the resulting solution to a 125-mL separatory funnel marked at approximately 50 mL and, if necessary, dilute the solution to the mark with 2.8 M sulphuric acid (Note 8). Add 0.2 g of ascorbic acid (Note 9) and mix the solution thoroughly, then add 20 mL of 5.3 M potassium iodide solution and 15 mL of toluene. Close the funnel and shake it for 2 min. Allow several minutes for the layers to separate, then drain the lower aqueous layer into a second 125-mL separatory funnel. Wash the stem of the first funnel with 2.8 M sulphuric acid added from a plastic wash-bottle and collect the washings in the second funnel. Add about 1 mL of 5.3 M potassium iodide solution to the first funnel containing the extract and, without mixing, drain the resulting aqueous layer into the second funnel (Note 10). Wash the stem of the first funnel with 2.8 M sulphuric acid again. Add 10 mL of toluene to the second funnel and extract the solution again by shaking it for 2 min. Drain off and discard the aqueous phase. Add the second extract to the first extract and, while the stem of the second funnel is in the neck of the first funnel, wash down the sides of the funnel with toluene added from a plastic wash-bottle. Drain off and discard the residual aqueous phase remaining in the first funnel, then add 10 mL of freshly prepared 1.5 M potassium iodide-2 M sulphuric acid solution, close the funnel and gently invert it 6-8 times. Drain off and discard the aqueous layer. Repeat the washing step, then drain off the aqueous layer and wash the stem of the funnel to remove the residual wash solution.

Add 10 mL of 2% sodium hydroxide solution to the combined extracts, then close the funnel and shake it for 1 min. Allow the layers to separate, then drain the lower aqueous layer into a 100-mL teflon beaker and wash the stem of the funnel with water. Strip the extract two more times by shaking it for 30 s each time with 5-mL portions of 2% sodium hydroxide solution and combine the aqueous layers with the first aqueous layer (Note 11).

If the aliquot taken for the extraction contained more than 30 µg of tin, evaporate the resulting sample and blank solutions to about 30 mL and cool them to room temperature. Transfer the solutions to volumetric flasks of appropriate size - 50-500 mL - and dilute them to volume with water. Transfer a suitable identical 10-20-mL aliquot of each solution to 100-mL beakers and, if necessary, dilute them to 20 ± 0.5 mL with water. In succession, add 2 mL of concentrated hydrochloric acid, 5 mL of 40% monochloroacetic acid solution and 2 mL of 5% ascorbic acid solution to each solution. Mix the solutions thoroughly, then add 2 mL of concentrated ammonium hydroxide, cool the solutions to room temperature in a water-bath and proceed with the pH adjustment, the complex formation and the extraction of the tin-gallein complex as described above. Measure the absorbance of the sample extract against the reagent blank extract and determine the tin content of the aliquot by reference to the calibration curve.

If the aliquot taken for the extraction contained 30 µg or less of tin, carefully evaporate the sample and blank solutions until sodium salts start to form (Note 12). Cool the beakers and add 20 mL of 10% hydrochloric acid and the recommended volumes of monochloroacetic acid and ascorbic acid solutions, then add 1 mL of concentrated ammonium hydroxide instead of 2 mL and proceed with the complex formation and the subsequent determination of tin as described above.

NOTES

1. The pH meter used should be capable of measuring pH to within ± 0.01 divisions. Because of the high absorbance exhibited by gallein - approximately 0.24 in a 10-mm cell under the conditions described - in the range of pH required for the formation of the tin complex, erratic results will be obtained for tin if the volume of gallein solution is not rigidly controlled and if the pH of the tin solutions deviates by more than approximately ± 0.01 units from that of the reagent blank solution.
2. The volume of the aqueous phase before

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

3. The absorbance of the n-amyl alcohol extract of the tin-gallein complex remains constant for at least 3 h.
4. If silicon is absent in copper-base alloys, use a pyrex beaker and omit the addition of hydrofluoric acid.
5. For iron and steel samples, hydrofluoric acid can be omitted and the sample can be decomposed as described in a pyrex beaker. However, any insoluble material present must be treated as follows:

   Dilute the solution obtained after the removal of nitric acid by evaporation of the solution to fumes of sulphur trioxide to about 100 mL with water, then using Whatman No. 541 paper, filter the solution into a 600-mL beaker. Wash the beaker and the paper and the residue thoroughly with water. Transfer the paper to a 30-mL zirconium crucible, burn off the paper at a low temperature and ignite the residue at about 600°C. Cool the crucible and fuse the residue with 1 g of sodium peroxide, then cool the crucible and transfer it to the covered beaker containing the initial filtrate. When the melt has dissolved, remove the crucible after washing it thoroughly with water, then cover the beaker and evaporate the solution to about 125 mL. Remove the cover, evaporate the solution to fumes of sulphur trioxide, then proceed as described.
6. If the sample contains lead, lead sulphate may precipitate after the filtration and dilution of the solution. The solution can be allowed to stand until the precipitate has settled, or a suitable portion can be filtered through a dry Whatman No. 42 filter paper.
7. If the sample contains tungsten, any insoluble tungsten compounds that precipitate after the filtration and dilution of the solution to volume can be removed before the extraction of tin iodide by filtering a suitable portion of the solution as described in Note 6.
8. The aliquot taken for extraction should not contain more than about 1 mg of tin.
9. The addition of ascorbic acid is not necessary if the sample contains very little iron.
10. By this procedure, the aqueous phase that remains in the bore of the stop-cock is transferred to the second funnel.
11. The toluene can be used for subsequent extractions if the toluene phases are combined in a large separatory funnel and washed twice by shaking with about 3% sodium hydroxide solution and then washed 3 times by shaking with 10% sulphuric acid.
12. A low result may be obtained for tin if the solution is allowed to evaporate to dryness and the resultant salts are heated strongly.

ACCURACY

Illustrated in Table 21 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine tin in nickel-base alloys.

REFERENCES

1. Donaldson, E.M. "Determination of tin in ores, steel and alloys with gallein after extraction as the iodide"; Mineral Sciences Division Bulletin TB 195; Mines Branch, Energy, Mines and Resources Canada; 1974.

2. Byrne, A.R. and Gorenc, D. "The toluene extraction of some elements as iodides from sulfuric acid-potassium iodide media. Application to neutron activation analysis - Part I: extraction behaviour of As, Au, Bi, Br, Cd, Cu, Ga, Ge, In, Hg, Mo, Pb, Sb, Se, Sn, W and Zn"; Anal Chim Acta 59:81-89; 1972.

3. Heegn, H. "Spectrophotometric determination of small tin content in ores and dressing products"; Freiberg Forschungsh A 455:47-61; 1969.

4. Mah, D.C. and Tupper, W.M. "The gallein colorimetric method for determining tin: an evaluation"; Department of Geology Paper 66-2; Carleton University (Canada); 1966.

5. Wood, G.A. "A rapid method for the determination of small amounts of tin in soils"; Imp Coll Sci and Technology, Geochem Prospecting Res Centre (London) Technical Communication No. 11; 1956.

6. McDonald, A.J. and Stanton, R.E. "The spectrophotometric determination of tin in soil with gallein"; Analyst 87:600-608; 1962.

7. Donaldson, E.M. "Determination of tin in ores, steel and alloys by atomic-absorption spectrophotometry after separation by extraction as the iodide"; Talanta 27:499-505; 1980.

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM IN HIGH-PURITY MOLYBDENUM AND TUNGSTEN METALS, IRON, STEEL, ALUMINUM METAL AND ALUMINUM- AND NICKEL-BASE ALLOYS WITH DIANTIPYRYLMETHANE

PRINCIPLE

Titanium is separated from a large amount of molybdenum or tungsten (viz. molybdenum and tungsten metals) by chloroform extraction of its cupferron complex from an ammoniacal - pH 8 - medium containing ammonium tartrate and ethylenediaminetetraacetic acid (EDTA) as complexing agents (1). It is separated from a large amount of aluminum (viz. aluminum metal and alloys) by chloroform extraction as the cupferrate from a 5% sulphuric acid medium. Iron, nickel and other elements (viz. iron, steel and nickel- and aluminum-base alloys) are separated from titanium by electrolysis with a mercury cathode in a 5% perchloric or sulphuric acid medium (2). Titanium is ultimately determined spectrophotometrically by measuring the absorbance at 390 nm of the yellow 1:3 titanium (IV)-diantipyrylmethane complex formed in a 1 M hydrochloric acid medium. The molar absorptivity of the complex at this wavelength is 1.48×10^3 $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCES

Coloured ions - chromium (III), chromium (VI), copper (II), cobalt, nickel and molybdenum, elements that cannot be kept in solution during complex formation - e.g., tungsten - and iron (III) and vanadium (V), which form coloured complexes with diantipyrylmethane in a 1 M hydrochloric acid medium, interfere in the determination of titanium with diantipyrylmethane (1).

In the method for molybdenum and tungsten metals, interference from all the above elements except iron is avoided by separating titanium from them and from various other elements - e.g., zinc, cadmium, bismuth and phosphate - by chloroform extraction of its cupferron complex from an ammoniacal medium containing ammonium tartrate and EDTA as complexing agents. Manganese interferes in the extraction of titanium because it is air-oxidized to manganese (III) in alkaline media. This subsequently causes incomplete extraction of titanium presumably because it is catalytically reduced to titanium (III). This interference is eliminated by extracting titanium from a reducing, sodium sulphite medium. Iron is partly coextracted as its cupferron complex under the conditions used for the separation of titanium. However, interference from coextracted iron (III) is eliminated by reducing it to iron (II) with ascorbic acid before complex formation. Up to 20 mg of iron, and up to at least 5 mg each of zirconium, thorium, tin (IV), aluminum and antimony (III), which are also partly coextracted, can be present during complex formation without affecting the titanium result (1,3).

In the method for iron, steel and nickel-base alloys, interference from iron and from coloured ions is avoided by separating them from titanium by electrolysis with a mercury cathode. In the methods for aluminum metal and alloys, titanium is separated from aluminum and from chromium, cobalt and nickel by chloroform extraction of its cupferron complex from a dilute sulphuric acid medium. Iron (III), copper (II) and vanadium (V) are also coextracted under these conditions but more than trace amounts are not usually present in high-purity aluminum metal. Iron and copper in aluminum alloys are separated from titanium by the mercury cathode separation step (2). Vanadium is not separated from titanium by this procedure, and more than approximately 1 mg will interfere during complex formation (3). Up to at least 3 mg of copper (II) (2) and up to 1 mg of cobalt, nickel or molybdenum can be present during complex formation without producing significant error in the titanium result (3).

RANGE

This method is suitable for molybdenum, tungsten and aluminum metals containing approximately 0.0005 to 0.2% of titanium, and for iron, steel and aluminum- and nickel-base alloys containing up to approximately 3%.

APPARATUS

MERCURY CATHODE.

REAGENTS

STANDARD TITANIUM SOLUTION, 0.2 mg/mL. Dissolve 0.1668 g of pure titanium dioxide by heating it in a 125-mL Erlenmeyer flask with 8 g of ammonium sulphate and 25 mL of concentrated sulphuric acid. Cool the solution, then using 5% sulphuric acid to wash the flask, transfer the solution to a 500-mL volumetric flask containing about 350 mL of water. Dilute the solution to approximately 480 mL with 5% sulphuric acid, then cool it to room temperature and dilute it to volume with the same acid solution. Prepare a 10-μg/mL solution by diluting 10 mL of this stock solution to 200 mL with 5% sulphuric acid. Prepare the diluted solution fresh as required.

DIANTIPYRYLMETHANE SOLUTION, 3% *m/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, then filter the solution and dilute it to 200 mL with water. Prepare a fresh solution every two days.

ASCORBIC ACID SOLUTION, 10% *m/V*. Prepare a fresh solution every two days.

EDTA, disodium salt solution, 10% *m/V*. Dissolve 20 g of the reagent in about 150 mL of hot water, then cool the solution and dilute it to 200 mL.

AMMONIUM TARTRATE SOLUTION, 25% *m/V*.

HYDROCHLORIC ACID, 9 M. Dilute 385 mL of concentrated hydrochloric acid to 500 mL with water.

CUPFERRON SOLUTION, 5% *m/V*. Prepare the solution fresh as required and filter it if necessary.

SODIUM SULPHITE SOLUTION, 10% *m/V*. Prepare the solution fresh as required.

SULPHURIC ACID, 5 and 50% *V/V*.

PERCHLORIC ACID, 5% *V/V*.

SODIUM HYDROXIDE SOLUTIONS, 25 and 50% *m/V*.

HYDROCHLORIC ACID, 25% *V/V*.

CHLOROFORM. 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, then using a pH meter, adjust the pH of each of the resulting solutions to 6.5 ± 0.5 (Note 1) with concentrated ammonium hydroxide. Add 10 mL of 9 M hydrochloric acid to each solution, then transfer them to 100-mL volumetric flasks and cool them to room temperature. Add 10 mL of 3% diantipyrylmethane solution, dilute the solutions to volume with water, mix them thoroughly and allow them to stand for at least 30 min to complete the complex formation (Note 2). Measure the absorbance of each solution at 390 nm against the blank solution as the reference solution, using 10-mm cells. Plot micrograms of titanium vs absorbance.

PROCEDURES

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

A - Molybdenum and tungsten metals

Transfer 0.25-0.5 g of powdered sample containing up to 0.5 mg of titanium to a 250-mL teflon beaker. Add 5 mL each of water and 50% sulphuric acid, then cover the beaker with a teflon cover and add 2 mL each of concentrated hydrofluoric, nitric and hydrochloric acids. Heat the solution gently until the sample has dissolved and

the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution and wash down the sides of the beaker with 5% sulphuric acid. Evaporate the solution to fumes of sulphur trioxide again to ensure the complete removal of hydrofluoric acid (Note 3), then cool it to room temperature.

In succession, add about 5 mL of 5% sulphuric acid, 10 mL of 25% ammonium tartrate solution, 5 mL of 10% EDTA solution, 10 mL of 10% sodium sulphite solution and a small piece of red litmus paper to the resulting solution. Neutralize the solution approximately with 50% sodium hydroxide solution (Note 4) and allow it to cool to room temperature. Using a pH meter, adjust the pH of the solution to 8.0 ± 0.1 with 25% sodium hydroxide solution and with 25% hydrochloric acid if required, then transfer the solution to a 125-mL separatory funnel and add 10 mL of 5% cupferron solution (Notes 5 and 6). Mix the solution thoroughly, then add 5 mL of chloroform, close the funnel and shake it for 2 min. Allow several minutes for the layers to separate, then drain the chloroform extract into a 100-mL beaker. Extract the solution three more times using 5 mL of chloroform and shaking it for 2 min each time (Note 7). Combine these extracts with the first extract and evaporate the resulting extract to dryness in a hot water-bath. Add 5 mL each of 50% sulphuric acid, water and concentrated hydrochloric and nitric acids to the 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 the solution and wash down the sides of the beaker with a small amount of 5% sulphuric acid and evaporate the solution to fumes of sulphur trioxide again.

If the sample contains 75 µg or less of titanium, dilute the resulting sample and blank solutions by adding approximately 5 mL of 5% sulphuric acid. Add 2 mL of 25% ammonium tartrate solution and 5 mL of 10% ascorbic acid solution to each solution, then proceed with the neutralization of the solutions (Note 9) and 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 sample solution by reference to the calibration curve.

If the sample contains more than 75 µg of titanium, dilute the sample and blank solutions by adding approximately 10 mL of 5% sulphuric acid. If necessary, filter the solutions - using Whatman No. 40 paper - into 50-mL volumetric flasks using 5% sulphuric acid to wash the beaker and the paper, then dilute them to volume with the same acid solution. Trasnfer an identical 5- or 10-mL aliquot of each solution to 100-mL beakers, add sufficient 50% sulphuric acid - i.e., 4 or 3 mL, respectively - so that approximately 2.5 mL of the concentrated acid will be present (Note 10), then proceed with the complex formation and the subsequent determination of the titanium content of the aliquot as described above.

B - Iron, steel and nickel-base alloys

Decompose 0.25-0.5 g of sample containing up to 7.5 mg of titanium as described in Procedure A, using 5 mL of concentrated perchloric acid instead of sulphuric acid (Note 11). Evaporate the solution to fumes of perchloric acid twice, after washing down the sides of the beaker with 5% perchloric acid, to ensure the complete removal of hydrofluoric acid, then add about 50 mL of water and heat the solution gently to dissolve the salts. If necessary, filter the solution - using Whatman No. 40 paper - into a mercury cathode cell to remove any graphitic carbon or tungsten trioxide present. Use 5% perchloric acid to wash the beaker and the paper, then discard the paper. Dilute the solution to about 75 mL with 5% perchloric acid, then electrolyze it for 45 min at about 10 A. Using Whatman No. 541 paper, filter the electrolyte into a 250-mL beaker using 5% perchloric acid to wash the cathode cell and the paper. Add 5 mL of concentrated hydrochloric acid to the filtrate and evaporate the solution until only a few drops of perchloric acid remain. Add 5 mL of 50% sulphuric acid and evaporate the solution to fumes of sulphur trioxide, then proceed with the complex formation and the subsequent determination of titanium as described in Procedure A, except that for samples containing more

than 75 µg of titanium dilute the final solution to 50-500-mL depending on the expected titanium content.

C - Aluminum metal

Transfer 0.25-0.5 g of sample to a 250-mL beaker, then cover the beaker and add 10 mL each of water and 50% sulphuric acid and 2 mL each of concentrated nitric and hydrochloric acids. Heat the mixture until the sample has dissolved and the evolution of oxides of nitrogen ceases, then remove the cover and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool the solution, wash down the sides of the beaker with 5% sulphuric acid and evaporate the solution to fumes of sulphur trioxide again. Cool the solution, add about 50 mL of water and, if necessary, heat the solution gently to dissolve the salts.

Cool the resulting solution to 10-15°C in an ice-bath (Note 12), then transfer it to a 125-mL separatory funnel using cold 5% sulphuric acid to wash the beaker. Dilute the solution to about 100 mL with the same acid solution and add sufficient cold 5% cupferron solution (Note 13) to precipitate titanium and iron. Mix the solution thoroughly, then add 5 mL of chloroform, close the funnel and shake it for 1 min. Allow several minutes for the layers to separate, then drain the chloroform extract into a 100-mL beaker. Extract the solution once more in a similar manner using 1 or 2 mL of cupferron solution (Note 14) and 5 mL of chloroform, then extract it two or more times by shaking it for about 30 s each time with 5-mL portions of chloroform until the organic layer is colourless. Combine the resulting extracts with the first extract and evaporate the solution to dryness in a water-bath. Add 5 mL each of concentrated nitric and perchloric acids to the residue, then cover the beaker and boil the solution to destroy organic material. Remove the cover and evaporate the solution until only a few drops of perchloric acid remain. Add 5 mL of 50% sulphuric acid, evaporate the solution to fumes of sulphur trioxide, then depending on the expected titanium content, proceed with the complex formation and the subsequent determination of titanium as described in Procedure A.

D - Aluminum-base alloys

Decompose 0.25-0.5 g of sample, contained in a 250-mL teflon beaker and containing up to 7.5 mg of titanium, by the method described in Procedure C and add 2 mL of concentrated hydrofluoric acid to dissolve any silicon present. After evaporating the solution to fumes of sulphur trioxide twice to ensure the complete removal of hydrofluoric acid, dissolve the salts in 50 mL of water as described in Procedure C, then transfer the resulting solution to a mercury cathode cell using 5% sulphuric acid to wash the beaker. Dilute the solution to about 75 mL with the same acid solution, then proceed with the mercury cathode separation as described in Procedure B. Using Whatman No. 541 paper, filter the electrolyte into a 250-mL beaker using 5% sulphuric acid to wash the cathode cell and the paper. Evaporate the resulting solution to about 50 mL, then cool it to 10-15°C in an ice-bath, transfer it to a 125-mL separatory funnel and proceed with the cupferron-chloroform extraction step and the subsequent determination of titanium as described in Procedure C.

NOTES

1. This pH adjustment is adequate even though the solution becomes hot.
2. The titanium-diantipyrylmethane complex formed under these conditions is stable for at least three days (1).
3. At this stage tungsten is present as insoluble yellow hydrated tungsten trioxide.
4. If the tungsten solution is slightly cloudy, heat it gently until it is clear.
5. Up to at least 0.5 mg of titanium can be separated from large amounts of molybdenum and tungsten and from various other elements by the cupferron-chloroform extraction step (1). A larger amount can probably be extracted if more cupferron is used 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 before complex formation (Note 10). Sulphuric acid or other acid solutions of titanium should not be evaporated to dryness or to near dryness. This can cause a low result for titanium because the salts are not readily redissolved (4).
9. If the solution is not completely clear after the pH has been adjusted to 6.5 ± 0.5 and the resulting solution has been acidified with 9 M hydrochloric acid, it can be clarified by filtering it before adding diantipyrylmethane solution.
10. If the resulting solution contains less than approximately 2.5 mL of concentrated sulphuric acid, a slightly low result will be obtained for titanium presumably because it is partly hydrolyzed during the pH adjustment step (1).
11. Perchloric acid is recommended instead of sulphuric acid because chromium perchlorate is more soluble than the sulphate.
12. The chloroform, cupferron solution and 5% sulphuric acid should also be cooled in an ice-bath.
13. Approximately 4-5 mL of 5% cupferron solution is usually sufficient for the complexation of 10 mg of metal ion (Note 14).
14. Complete precipitation of iron and titanium is indicated by a transient white precipitate resulting from the presence of excess cupferron.

ACCURACY

Illustrated in Tables 22 and 23 in Appendix A.

OTHER APPLICATIONS

Procedure B can be used to determine titanium in nickel oxide.

REFERENCES

1. Donaldson, E.M. "Determination of titanium in high-purity molybdenum and tungsten metals with diantipyrylmethane after separation by extraction of its cupferron complex"; Talanta 16:1505-1511; 1969.

2. Rolko, V.H.E. "Spectrophotometric determination of titanium in iron, steel, non-ferrous alloys and silicate rocks with diantipyrylmethane"; Mineral Sciences Division Report MRP/MSL 80-105 (IR); Mines Branch, Energy, Mines and Resources Canada; 1980.

3. Donaldson, E.M. "Methods for the analysis of ores, rocks and related materials"; Mines Branch Monograph 881; Mines Branch, Energy, Mines and Resources Canada; 105-109; 1974.

4. Hillebrand, W.F., Lundell, G.E.F., Bright, H.A. and Hoffman, J.I. "Applied inorganic analysis" (2nd ed); New York, Wiley; 577; 1953.

SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN IN IRON AND STEEL BY CHLOROFORM EXTRACTION OF THE TUNGSTEN-THIOCYANATE-DIANTIPYRYLMETHANE COMPLEX

PRINCIPLE

Molybdenum is separated from tungsten, if necessary, by chloroform extraction as the xanthate from a 1.5 M hydrochloric acid medium and tungsten is subsequently reduced to tungsten (V) with stannous chloride in a 3.6 M sulphuric acid-5.8 M hydrochloric acid medium. It is ultimately determined spectrophotometrically by measuring the absorbance at 404 nm of the yellow tungsten (V)-thiocyanate-diantipyrylmethane complex, after extraction of the complex into chloroform from a 2.4 M sulphuric acid-7.8 M hydrochloric acid medium containing ammonium hydrogen fluoride. The molar absorptivity of the complex in chloroform at this wavelength is 1.51×10^3 $L.mol^{-1}.mm^{-1}$ (1).

INTERFERENCES

Up to at least 10 mg of cobalt (II), vanadium (V), uranium (VI), niobium (V), nickel, bismuth, copper (II), antimony (V), aluminum, manganese (II), titanium (IV), zirconium, cadmium, chromium (VI), arsenic (III), tellurium (IV) and phosphorus (V), and up to 50 mg of iron (III) and 20 mg of zinc do not interfere in the extraction and subsequent determination of tungsten. Arsenic and tellurium are reduced to the elemental state during the reduction of tungsten with stannous chloride. However, interference from the resulting precipitates during the extraction of tungsten can be avoided by filtering the solution through glass-wool before the extraction step. Copper, in large amounts, interferes during extraction because it precipitates as cuprous thiocyanate (1). Interference from niobium and titanium, which form coloured extractable thiocyanate complexes (2,3), is avoided by complexing them with ammonium hydrogen fluoride before the formation of the tungsten complex (1).

Up to 0.25 mg of molybdenum can be present in the aliquot taken for extraction without causing error in the tungsten result. Interference from a larger amount of molybdenum is eliminated by separating it from tungsten by chloroform extraction of its ethyl xanthate complex from a 1.5 M hydrochloric acid medium. Selenium, which also interferes, is also separated from tungsten by this procedure. Cobalt (II), bismuth, nickel, vanadium (V), iron (III) and tin (IV) are partly extracted as xanthate complexes, and arsenic (III), tellurium (IV) and antimony (III) are completely extracted under these conditions (1,4). Copper forms a bright yellow precipitate that remains above the chloroform layer. However, the precipitate is decomposed completely when the aqueous layer is subsequently heated to destroy the excess xanthate (1).

RANGE

This method is suitable for samples containing approximately 0.002 to 6% of tungsten but material containing higher concentrations can also be analyzed with reasonable accuracy.

APPARATUS

POLYPROPYLENE SEPARATORY FUNNELS. 125-mL pear-shape type.

REAGENTS

STANDARD TUNGSTEN SOLUTION, 1 mg/mL. Dissolve 0.8973 g of sodium tungstate dihydrate in water and dilute the solution to 500 mL. Prepare a 25-µg/mL solution by diluting 5 mL of this stock solution to 200 mL with water. Prepare the diluted solution fresh as required.

DIANTIPYRYLMETHANE SOLUTION, 1% *m/V* in 20% hydrochloric acid. Dissolve 0.5 g of 4,4'-methylenediantipyrine in 25 mL of water containing 10 mL of concentrated hydrochloric acid and dilute the solution to 50 mL with water. Prepare a fresh solution every two days.

STANNOUS CHLORIDE SOLUTION, 45% *m/V*. Dissolve 22.5 g of stannous chloride dihydrate in concentrated hydrochloric acid and dilute the solution to 50 mL with concentrated hydrochloric acid. Prepare the solution fresh as required.

POTASSIUM THIOCYANATE SOLUTION, 20% *m/V*. Prepare a fresh solution every seven days.

POTASSIUM ETHYL XANTHATE SOLUTION, 20% *m/V*. Prepare the solution fresh as required.

AMMONIUM HYDROGEN FLUORIDE SOLUTION, 10% *m/V*.

TARTARIC ACID SOLUTIONS, 7.5 and 50% *m/V*.

SODIUM HYDROXIDE SOLUTION, 50% *m/V*.

HYDROCHLORIC ACID, 8 M. Dilute 340 mL of concentrated hydrochloric acid to 500 mL with water.

CHLOROFORM CONTAINING 1% *V/V* OF CONCENTRATED THIOGLYCOLLIC ACID. Prepare the solution fresh as required.

CHLOROFORM. Reagent-grade.

CALIBRATION CURVES

By burette, add 1, 2, 4, 6, 8 and 12 mL of the dilute standard 25-µg/ML tungsten solution to six 125-mL Erlenmeyer flasks 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 the solutions thoroughly after each addition, then place the flasks in a water-bath maintained at about 100°C for 30 min. Remove the flasks and cool the solutions to 10-15°C in an ice-bath.

Transfer the resulting solutions to 125-mL polypropylene separatory funnels marked at approximately 75 mL and wash each flask 3 times with cold, concentrated hydrochloric acid added from a plastic wash-bottle. Add the washings to the corresponding funnels and dilute the solutions to the mark with cold, concentrated hydrochloric acid. In succession, add 10 mL of 10% ammonium hydrogen fluoride solution, 10 mL of 20% potassium thiocyanate solution (Note 1) and 2 mL of 1% diantipyrylmethane solution to each funnel and mix the solutions thoroughly. Add 10 mL of chloroform containing 1% thioglycollic acid (Note 2), then close each funnel tightly and shake it for 2 min. Allow several minutes for the layers to separate, then drain the chloroform layer into a 60-mL glass separatory funnel. Extract the solution two more times in a similar manner using 0.5 mL of diantipyrylmethane solution each time and 5- and 3-mL portions of chloroform, respectively (Note 3), then wash the aqueous phase by shaking it for 30 s with 3 mL of chloroform. Add these extracts to the first extract, then add 10 mL of 8 M hydrochloric acid to the resulting extract and shake the funnel for about 30 s (Note 4). Allow several minutes for the layers to separate, then filter the chloroform extract through a thick wad of cotton-wool into a dry 25-mL volumetric flask. Wash the aqueous layer twice with 2- or 3-mL portions of chloroform containing thioglycollic acid. Filter the washings into the volumetric flask and dilute the extract to volume with chloroform containing thioglycollic acid (Note 5). Measure the absorbance of the blank extract and of each of the four extracts of lowest tungsten content (Note 6) at 404 nm against chloroform containing thioglycollic acid as the reference solution, using 20-mm cells. Measure the absorbance of the blank extract and of each of the five extracts of highest tungsten content in a similar manner, using 10-mm cells. Correct the absorbance value obtained for each tungsten-thiocyanate-diantipyrylmethane extract by subtracting the corresponding blank value. Plot micrograms of tungsten vs absorbance for each series of measurements.

PROCEDURES

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

Low molybdenum content

Transfer 0.2-1 g of sample to a 400-mL beaker, add 20 mL of concentrated hydrochloric

acid, then cover the beaker and heat the mixture gently until the sample has dissolved. Add 5 mL of concentrated nitric acid and heat the solution until any carbides present are decomposed. Remove the cover, add 3 or 4 drops of concentrated hydrofluoric acid and evaporate the solution to dryness to remove nitric acid. Add 5 mL of concentrated hydrochloric acid and about 25 mL of water to the beaker and heat the solution gently to dissolve the salts. Add 30 mL of 50% tartaric acid solution, cool the solution to room temperature and carefully add 25 mL of 50% sodium hydroxide solution. Cool the solution to room temperature, transfer it to a 200-mL volumetric flask and dilute it to volume with water (Notes 7 and 8).

Transfer a 4-10-mL aliquot of the resulting solution, containing not more than 0.25 mg of molybdenum, to a 125-mL Erlenmeyer flask. Transfer an identical aliquot of the blank solution to another flask. Dilute each solution to approximately 15 mL with water and proceed with the reduction and the extraction of tungsten as described above. Measure the absorbance of the blank and sample extracts as described above, using 10- or 20-mm cells as required. Correct the absorbance value obtained for the sample extract by subtracting that obtained for the reagent blank extract and determine the tungsten content of the aliquot by reference to the appropriate calibration curve.

High molybdenum content

If the aliquot to be taken for analysis contains more than 0.25 mg of molybdenum, transfer suitable identical aliquots of the blank and sample solutions to 60-mL separatory funnels marked at 25 mL. Add 4.5 mL of 8 M hydrochloric acid to each funnel and dilute the solutions to the mark with water. Add 10 mL of chloroform to each funnel, then add 2 mL of freshly prepared 20% potassium ethyl xanthate solution (Note 9), close the funnels and extract immediately (Note 10) by shaking the funnels for 1 min. Allow the layers to separate, then drain off and discard the chloroform layers. Continue to extract the solutions in a similar manner using 0.3-0.5-mL portions of xanthate solution and 5 mL of chloroform each time until the chloroform layer is colourless (Notes 11 and 12). Transfer the resulting aqueous layers to 125-mL Erlenmeyer flasks and heat the solutions gently to remove the residual chloroform. Evaporate the solutions to approximately 15 mL, then proceed with the reduction, the extraction and the subsequent determination of tungsten as described above.

NOTES

1. Sodium thiocyanate cannot be used instead of potassium thiocyanate because a dense white precipitate of sodium sulphate will form in the solution.
2. Thioglycollic acid is added to the chloroform to reduce interfering organic peroxides that would reoxidize the tungsten complex.
3. Because of the high acid content of the solution, some salts may precipitate during the extraction step. This does not interfere with the extraction of tungsten.
4. Shaking the extract with 8 M hydrochloric acid reduces turbidity after the extract is filtered and diluted to volume with chloroform containing thioglycollic acid.
5. If the blank or the tungsten extract is slightly opalescent, or becomes opalescent on standing, filter a suitable portion of the extract through two combined dry Whatman No. 42 filter papers before the spectrophotometric measurement.
6. The absorbance of the chloroform solution of the tungsten-thiocyanate-diantipyrylmethane complex remains constant for at least 24 h.
7. If a precipitate of hydrous oxides is present, allow it to settle before an aliquot is taken for the determination of tungsten.
8. If the sample is a high-tungsten steel, further dilution of the solution will be necessary before an aliquot can be taken for the tungsten determination. In this case, transfer suitable identical aliquots of the blank and sample solutions to 100-mL volumetric flasks, add 5 mL of 50% sodium hydroxide solution, dilute the solutions to volume with 7.5% tartaric acid solution, then proceed as described.

9. The xanthate solution should be added by pipette using a suction bulb or by using a graduated or marked medicine dropper and the extraction should be carried out in a fume hood. Prolonged exposure to xanthate vapour can produce an allergic reaction.
10. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.
11. A three-stage extraction with a total volume of 4 mL of 20% potassium ethyl xanthate solution is sufficient for the separation of 5 mg of molybdenum. It is also sufficient for the separation of 5 mg of arsenic, selenium or tellurium.
12. If the sample contains nickel, vanadium or cobalt, the extract obtained after the complete separation of the purple-red molybdenum complex will not be colourless. These elements are partly coextracted as xanthates which continue to colour the extract.

ACCURACY

Illustrated in Table 24 in Appendix A.

REFERENCES

1. Donaldson, E.M. "Spectrophotometric determination of tungsten in ores and steel by chloroform extraction of the tungsten-thiocyanate-diantipyrylmethane complex"; Talanta 22:837- 841; 1975.

2. Fogg, A.G., Marriott, D.R. and Burns, D.T. "The spectrophotometric determination of tungsten with thiocyanate - Part I: A review of procedures"; Analyst 95:848-853; 1970.

3. Elwell, W.T. and Wood, D.F. "Analytical chemistry of molybdenum and tungsten"; New York, Pergamon Press; 103; 1971.

4. Donaldson, E.M. "Chloroform extraction of metal ethyl xanthates from hydrochloric acid media"; Talanta 23:411-416; 1976.

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN IRON, STEEL AND ALUMINUM- AND NICKEL-BASE ALLOYS BY CHLOROFORM EXTRACTION OF THE N-BENZOYL-N-PHENYLHYDROXYLAMINE COMPLEX

PRINCIPLE

Chromium is separated from vanadium, if necessary, by electrolysis with a mercury cathode in a 2% perchloric acid medium. Vanadium is ultimately determined spectrophotometrically by measuring the absorbance at 475 nm of the red vanadium (V)-N-benzoyl-N-phenylhydroxylamine (NBPHA) complex, after extraction of the complex into chloroform from a 2 M sulphuric acid-4 M hydrofluoric acid medium containing ammonium persulphate as oxidant. The molar absorptivity of the complex at this wavelength is 4.28×10^2 $L.mol^{-1}.mm^1$ (1).

INTERFERENCES

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 or zirconium, and up to 50 mg of molybdenum or tungsten do not interfere in this method. Chromium and cerium interfere if they are present in the hexavalent and tetravalent states, respectively. Interference from up to approximately 10 mg of chromium or cerium is eliminated by reducing them to the trivalent state with iron (II). Vanadium is also reduced by iron (II) but it is subsequently reoxidized to vanadium (V) with ammonium persulphate. Chromium (III) and cerium (III) are not reoxidized under these conditions except possibly when silver is present. Interference from more than 10 mg of chromium is avoided by separating it from vanadium by electrolysis with a mercury cathode (1).

RANGE

This method is suitable for samples containing approximately 0.0005 to 0.15% of vanadium. However, material containing higher concentrations can also be analyzed if a suitable aliquot of a sulphuric acid solution of the sample is taken.

APPARATUS

MERCURY CATHODE.

POLYPROPYLENE SEPARATORY FUNNELS. 125-mL pear-shape type.

REAGENTS

STANDARD VANADIUM SOLUTION, 0.2 mg/mL. Dissolve 0.1785 g of pure vanadium pentoxide (Note 1) by heating it with 50 mL of 50% sulphuric acid and 5 mL of concentrated nitric acid. Evaporate the resulting solution to fumes of sulphur trioxide, then cool it to room temperature and dilute it to 500 mL with water. Prepare a 25-µg/mL solution by diluting 25 mL of this stock solution to 200 mL with water. Prepare the diluted solution fresh as required.

NBPHA SOLUTION, 0.1% *m/V* in chloroform. Store the solution in a brown bottle.

FERROUS AMMONIUM SULPHATE SOLUTION, 10% *m/V*. Dissolve 5 g of ferrous ammonium sulphate hexahydrate in about 30 mL of water containing 1 mL of 50% sulphuric acid and dilute the solution to 50 mL with water. Prepare the solution fresh as required.

AMMONIUM PERSULPHATE SOLUTION, 10% *m/V*. Prepare the solution fresh as required.

SULPHURIC ACID, 12.5 M. Add 695 mL of concentrated sulphuric acid -slowly and while stirring the solution - to 275 mL of water in a 1500-mL pyrex beaker. Allow the solution to cool to room temperature, then transfer it to a 1-L volumetric flask and dilute it to volume with water.

SULPHURIC ACID, 50% *V/V*.

HYDROFLUORIC ACID, 25 M. Dilute 218 mL of concentrated hydrofluoric acid to 250 mL with water in a plastic bottle.

CHLOROFORM, alcohol-free. Chromatoquality-reagent. Reagent-grade chloroform can be purified by washing it 5 or 6 times with water, then by distilling it after drying it 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. In succession, add 8 mL of 25 M hydrofluoric acid and 4 mL of 10% ferrous ammonium sulphate solution to each funnel, then dilute the solutions to approximately 40 mL with water and mix them thoroughly. Add 5 mL of 10% ammonium persulphate solution, dilute the solutions to the 50-mL mark with water and mix them thoroughly. Add 10 mL of 0.1% NBPHA-chloroform solution to each funnel, then close it and shake it for 2 min. 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. Extract the solution three more times in a similar manner using 5, 3 and 3 mL of NBPHA solution, respectively. Combine these extracts with the first extract, then wash the funnel and the cotton-wool with 1 or 2 mL of chloroform and dilute the extract to volume with chloroform (Note 2). Measure the absorbance of each of the resulting extracts at 475 nm against chloroform as the reference solution, using 20-mm cells. Correct the absorbance value obtained for each vanadium-NBPHA extract by subtracting that obtained for the blank extract. Plot micrograms of vanadium vs absorbance.

PROCEDURES

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

Chromium content 10 mg or less

Transfer 0.1-0.5 g of sample to a 250-mL teflon beaker and add 5 mL of water, 8 mL of 12.5 M sulphuric acid and 2 mL of concentrated hydrofluoric acid. Cover the beaker with a teflon cover, add 5 mL of concentrated nitric acid and heat the mixture gently until the sample has dissolved and the evolution of oxides of nitrogen ceases. Remove the cover and evaporate the solution to fumes of sulphur trioxide, then cool the solution and wash down the sides of the beaker with water. Evaporate the solution to fumes of sulphur trioxide again to ensure the complete removal of nitric acid. Cool the solution, add 5 mL of water and allow the solution to cool to room temperature (Note 3).

Just before the extraction step, add 8 mL of 25 M hydrofluoric acid (Note 4) to the resulting sample (Note 5) and blank solutions. Transfer the solutions to 125-mL polypropylene separatory funnels and, after the additions of the recommended volumes of iron (II) ammonium sulphate and ammonium persulphate solutions, proceed with the extraction of vanadium 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 reagent blank extract and determine the vanadium content of the sample extract by reference to the calibration curve.

Chromium content greater than 10 mg

Transfer 0.1-0.5 g of sample to a 250-mL teflon beaker, then cover the beaker with a teflon cover and add 5 mL each of water and concentrated perchloric, nitric and hydrochloric acids. Add 2 mL of concentrated hydrofluoric acid and heat the mixture gently until the sample has dissolved (Note 6) and the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution until copious fumes of perchloric acid are evolved. Cool the solution, add about 20 mL of water and, if necessary, heat the solution gently to dissolve the salts. If necessary, filter the solution - using Whatman No. 40 paper -

into a mercury cathode cell and wash the beaker and the paper with water. Discard the paper. Dilute the resulting solution to about 200 mL with water and electrolyze it for 45 min at about 10 A. Using Whatman No. 541 paper, filter the electrolyte into a 400-mL pyrex beaker and wash the cathode cell and the paper with water. Discard the paper and evaporate the filtrate to dryness. Wash down the sides of the beaker with water, add 8 mL of 12.5 M sulphuric acid and evaporate the solution to fumes of sulphur trioxide. Cool the solution, add 5 mL of water and allow the solution to cool to room temperature. Transfer the solution to a 125-mL polypropylene separatory funnel, add 8 mL of 25 M hydrofluoric acid and the recommended volumes of iron (II) ammonium sulphate and ammonium persulphate solutions, then proceed with the extraction and the subsequent determination of vanadium as described above.

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 about 10 mL of water and 6 mL of 50% sulphuric acid and heat the mixture until the oxide has dissolved. Dilute the solution to about 125 mL with water, then add 1 g of sodium sulphite in small portions to reduce vanadium to vanadium (IV). Boil the solution in the open beaker for 15-20 min to expel the excess sulphur dioxide. While the solution is hot, titrate it with standard 0.1 N (0.02 M) potassium permanganate solution (1 mL = 5.094 mg of vanadium), which has been previously standardized against sodium oxalate (4), until the colour of the solution just changes from a pure yellow. Correct the result obtained by subtracting that obtained for a blank solution that is carried through the same procedure.

   Then,

$$\% \text{ V} = \frac{(\text{V} - \text{v}) \times \text{N} \times 50.94}{\text{mass of } \text{V}_2\text{O}_5 \text{ taken (mg)}} \times 100$$

   where:

   V = volume (mL) of potassium permanganate solution required by the vanadium pentoxide

   v = volume (mL) of potassium permanganate solution required by the blank solution

   N = normality of the potassium permanganate solution

   Subsequently, the mass (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 used to prepare the standard vanadium solution. However, the purity of the reagent should be checked as described above.

2. The absorbance of the chloroform extract of the vanadium-NBPHA complex remains constant for at least 24 h.

3. Samples containing more than 0.15% of vanadium can be analyzed 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. 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 before the extraction of vanadium.

4. The hydrofluoric acid must be added just before the extraction step because it volatilizes from the solution if the solution is allowed to stand for some time at room temperature.

5. If graphitic carbon is present, filter the resulting sample solution into the separatory funnel using Whatman No. 40 paper and a plastic funnel.

6. More hydrochloric and nitric acids may be required to obtain complete dissolution.

ACCURACY

Illustrated in Table 25 in Appendix A.

OTHER APPLICATIONS

This method can be used to determine vanadium in high-purity niobium, tantalum, titanium and zirconium metals and in cobalt and nickel arsenides.

REFERENCES

1. Donaldson, E.M. "Determination of vanadium in refractory metals, steel, cast iron, alloys and silicates by extraction of an NBPHA complex from a sulphuric-hydrofluoric acid medium"; Talanta 17:583-591; 1970.

2. Priyadarshini, U. and Tandon, S.G. "Spectrophotometric determination of vanadium (V) with N-benzoyl-N-phenylhydroxylamine"; Anal Chem 33:435-438; 1961.

3. Hillebrand, W.F., Lundell, G.E.F., Bright, H.A. and Hoffman, J.I. "Applied inorganic analysis" (2nd ed); New York, Wiley; 458-459; 1953.

4. Reference 3, pp 186-187.

ATOMIC-ABSORPTION DETERMINATION OF ZINC IN HIGH-PURITY NICKEL, MOLYBDENUM AND TUNGSTEN METALS AFTER SEPARATION BY EXTRACTION OF THE THIOCYANATE-DIANTIPYRYLMETHANE COMPLEX

PRINCIPLE

Zinc is separated from the matrix elements by chloroform extraction of the zinc thiocyanate-diantipyrylmethane ion-association complex at pH 3.25 from a citric acid medium containing thiourea and ammonium hydrogen fluoride or hydrofluoric acid as complexing agents. Zinc is subsequently back-extracted into dilute ammonium chloride-ammonium hydroxide solution and is ultimately determined by atomic-absorption spectrophotometry at 213.9 nm in an oxidizing air-acetylene flame in a 1% hydrochloric acid medium (1,2).

INTERFERENCES

As described in the atomic-absorption method for cobalt (p 42), up to 5 mg of iron (III) and 10 mg each of copper (II), cadmium, lead, manganese (II), vanadium (V), zirconium, titanium (IV), bismuth, tin (IV), antimony (V), chromium (III), chromium (VI), arsenic (V) and phosphorus (V) do not interfere in the extraction of zinc as its thiocyanate-diantipyrylmethane complex from solutions containing up to 1 g of nickel (1). Although 3 or 4 mg of iron (III) interfere in the extraction of cobalt from solutions containing large amounts of molybdenum and tungsten, and more than 0.5 mg of phosphorus (V) interferes in the extraction of cobalt from tungsten solutions, these amounts of iron and phosphorus do not interfere in the extraction of zinc from these solutions because it is extracted preferentially to cobalt. Up to at least 2 mg and 5 mg of phosphorus (V) do not interfere in the extraction of zinc from solutions containing 1 g of tungsten and molybdenum, respectively. Zinc is completely extracted from molybdenum and tungsten solutions containing at least 5 mg each of iron (III), copper (II), vanadium (V), titanium (IV), chromium (VI) and arsenic (V) and at least 10 mg each of the remaining elements mentioned above (2).

RANGE

This method is suitable for samples containing approximately 0.0001 to 0.1% of zinc.

REAGENTS

STANDARD ZINC SOLUTION, 100 µg/mL. Dissolve 0.1000 g of pure zinc metal in about 20 mL of water containing 5 mL of concentrated hydrochloric acid and evaporate the solution to dryness. Dissolve the salts in water and dilute the solution to 1 L. Prepare a 10-µg/mL solution by diluting 20 mL of this stock solution to 200 mL with water.

HYDROCHLORIC ACID, 1% *V/V*.

CALIBRATION SOLUTIONS

Add 1 mL of concentrated hydrochloric acid to six 100-mL volumetric flasks, then by burette, add to the first five flasks 1, 2, 4, 6 and 8 mL, respectively, of the dilute standard 10-µg/mL zinc solution. The contents of the last flask constitute the zero calibration solution. Dilute each solution to volume with water.

PROCEDURE

Following sample decomposition (Note 1) by the appropriate procedure described in the atomic-absorption method for cobalt (p 43), proceed with the extraction of zinc (Note 2) - and any cobalt present - and the ultimate treatment of the solution as described in the above method.

Measure the absorbance of the resulting sample and blank solutions at 213.9 nm in an oxidizing air-acetylene flame (Note 3). Determine the zinc contents, in milligrams, of the solutions

by relating the resulting values to those obtained concurrently for calibration solutions of slightly higher and lower zinc concentrations. Correct the result obtained for the sample solution by subtracting that obtained for the reagent blank solution.

NOTES

1. In this procedure a reagent blank, which is ultimately diluted to 25 mL, should be carried along with the samples.
2. Although the pH of the solution during the extraction step should be kept within the range 3.20-3.30 if both zinc and cobalt are to be determined, such rigid control of the pH is not necessary if only zinc is to be determined (1,2). Zinc is completely extracted in the pH range 1.4 to 3.9 (1). However, to minimize the coextraction of iron, which is not efficiently complexed with citric acid below approximately pH 3, it is recommended that the pH of the solution should be kept within the range 3.20-3.80 for the extraction of zinc.
3. If dilution of the solution is necessary, dilute a suitable aliquot to an appropriate volume with 1% hydrochloric acid.

ACCURACY

Illustrated in Table 26 in Appendix A.

OTHER APPLICATIONS

The method described for molybdenum and tungsten metals can be used to determine zinc in high-purity niobium and tantalum metals (2).

REFERENCES

1. Donaldson, E.M. and Rolko, V.H.E. "Determination of cobalt and zinc in nickel metal by atomic-absorption spectrophotometry after separation by simultaneous chloroform extraction of their thiocyanate-diantipyrylmethane complexes"; Mineral Sciences Division Bulletin TB 93; Mines Branch, Energy, Mines and Resources Canada; 1967.

2. Donaldson, E.M., Charette, D.J. and Rolko, V.H.E. "Determination of cobalt and zinc in high-purity niobium, tantalum, molybdenum and tungsten metals by atomic-absorption spectrophotometry after separation by extraction"; Talanta 16:1305-1310; 1969.

APPENDIX A

In the following tables the abbreviations NBS, BCS and CCRMP refer to the National Bureau of Standards, British Chemical Standards and Canadian Certified Reference Materials Project certified reference materials, respectively. The ranges given in the third column indicate the lowest and highest results obtained during the certification programs and used by the respective agencies for certification purposes. Except for the results given in Table 23 and some in Table 22 - indicated in the footnotes - all the remaining results are those obtained by the author during the respective method development work or during early collaborative work with the National Bureau of Standards in Washington, D.C. Unless otherwise indicated in the footnotes to the Tables, these results are taken from the pertinent paper(s) or report(s) by the author listed in the References at the end of each method.

Table 1 - Results obtained for aluminum in NBS and BCS iron, steel and ferrous and non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Al	Al found, %	
			Atomic-absorption spectrophotometry	Spectrophotometric pyrocatechol violet method
NBS-14e Basic open-hearth steel	0.4 Mn, 0.2 Si	0.059*	0.062	0.060
NBS-19g Acid open-hearth steel	0.6 Mn, 0.2 Si, 0.4 Cr, 0.03 Ti, 0.03 Nb	0.030	0.028, (0.028†)	0.027, 0.028
NBS-55c Open-hearth iron		0.003*	0.0016, 0.0011	0.0012, 0.0009
NBS-55e Open-hearth iron		0.002 (0.001-0.003)	0.0008, 0.0006, (0.0011, 0.0007†)	--
NBS-61 Ferrovanadium	31.2 V, 1.2 C, 3.6 Mn, 7.8 Si, 1.3 Ni, 0.7 Mo, 0.2 Ti, 0.2 P	0.02 (0.01-0.03)	0.021, 0.021	0.022
NBS-100A Manganese steel	0.4 C, 1.7 Mn, 0.2 Si	0.040 (0.039-0.042)	0.037, 0.037, (0.037†)	--
NBS-101F 18 Chromium-10 nickel steel	10.0 Ni, 18.5 Cr, 0.9 Si, 0.3 V (0.0007 Al)#	0.0057 §	0.0056	--
		0.0107 §	0.011_0	--
		0.0207 §	0.021_5	--
NBS-106B Chromium-molybdenum-aluminum steel	0.5 Mn, 0.3 Si, 1.2 Cr, 0.2 Mo	1.07 (1.06-1.09)	--	1.08_1
NBS-125 High silicon steel	0.1 Mn, 5.0 Si	0.261 (0.25-0.270)	0.266	0.263
NBS-170A Basic open-hearth steel	0.3 Mn, 0.3 Ti, 0.04 Zr	0.046 (0.036-0.058)	0.049, 0.048	0.046
BCS-326 Mild steel	0.3 Mn	0.005 (0.003-0.007)	--	0.0031, 0.0034
BCS-327 Mild steel	0.2 Mn, 0.1 V	0.020 (0.016-0.023)	0.019	0.017
BCS-328 Mild steel	0.4 Mn, 0.2 V	0.048 (0.045-0.053)	0.050	0.048
BCS-329 Mild steel	0.1 Mn, 0.1 V	0.058 (0.052-0.062)	0.059	0.059
NBS-62B Manganese bronze	57.4 Cu, 38.0 Zn, 1.3 Mn, 1.0 Sn	0.97 (0.94-0.98)	0.956, 0.943	0.975
NBS-158 Silicon bronze	90.9 Cu, 2.7 Si, 1.3 Mn, 1.0 Sn	0.54 (0.53-0.56)	0.536	0.539
NBS-162A Nickel-copper alloy	63.9 Ni, 30.6 Cu, 1.6 Mn, 0.9 Si	0.50 (0.49-0.50)	0.500	0.503
NBS-169 Electrical-heating alloy	77.2 Ni, 20.3 Cr, 1.4 Si, 0.04 Zr	0.095 (0.087-0.105)	0.095	--
NBS-349 Heat-resisting alloy	57.2 Ni, 19.5 Cr, 4.0 Mo, 3.1 Ti, 0.3 Si, 0.4 Mn, 14.0 Co, 0.08 Zr	1.23*	1.22_3	--
NBS-C1100 Cartridge brass	67.4 Cu, 32.2 Zn	0.008	0.0079	0.0075
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.0006	0.0002, 0.0002, 0.0002	--

*NBS provisional result.

†Results in brackets obtained after fusing the insoluble material with 1 g of a 75% sodium carbonate-25% boron trioxide mixture.

#Mean of two results - viz, 0.0006_5 and 0.0006_9% - by the atomic-absorption method.

§Value includes aluminum present # and that added to a 1-g sample.

Table 2 - Results obtained for aluminum in synthetic molybdenum and tungsten samples

Matrix*	Total Al present, %	Al found, %
Mo	0.0010	0.0009
	0.0050	0.0047
	0.0100	0.0098
	0.0250	0.024_8
	0.0500	0.050_6
	0.1000	0.099_5
W	0.0010	0.0012
	0.0050	0.0050
	0.0100	0.010_1
	0.0250	0.024_4
	0.0500	0.049_2
	0.1000	0.099_0

*The metals (0.5 g) used to prepare the synthetic samples were aluminum-free.

Table 3 - Results obtained for antimony in NBS and BCS non-ferrous alloys and in CCRMP commercial-purity copper rods

Sample	Nominal composition, %	Certified value and range, % Sb	Sb found, %	
			Spectrophotometric iodide method	Atomic-absorption spectrophotometry
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.012	0.012	0.011, 0.011
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.005	0.0049	0.0036
NBS-C1120 Aluminum brass C	80.1 Cu, 18.1 Zn, 1.5 Al, 0.09 As	0.100*	0.092, 0.091	0.095
NBS-62B Manganese bronze	57.4 Cu, 38.0 Zn, 1.3 Mn, 1.0 Al, 1.0 Sn, 0.8 Fe	0.005 (0.005-<0.01)†	0.011, 0.011	0.009
NBS-63c Phosphor bronze bearing metal	80.5 Cu, 9.4 Pb, 9.0 Sn, 0.2 P, 0.02 As	0.52 (0.50-0.54)	0.512, 0.510	0.513
NBS-127A Solder	30.0 Sn, ~70 Pb, 0.13 As, 0.04 Bi	0.79 (0.78-0.80)	0.791	0.797, 0.792#
BCS-183/1 Bronze	84.8 Cu, 5.0 Sn, 5.2 Zn, 3.5 Pb, 0.5 P, 0.14 As	0.24 (0.23-0.24)	0.234, 0.239	0.240
BCS-183/3 Leaded gunmetal	84.5 Cu, 6.7 Sn, 3.3 Zn, 3.4 Pb, 1.5 Ni, 0.15 As	0.25 (0.24-0.27)	0.252, 0.254	0.261
BCS-207/2 Gunmetal	87.3 Cu, 9.7 Sn, 1.6 Zn 0.7 Pb, 0.07 As, 0.04 Bi	0.10 (0.093-0.11)	0.093, 0.094	0.098
BCS-207 Bronze "C"	86.8 Cu, 9.8 Sn, 2.5 Zn 0.05 As	0.04 (0.03-0.05)	0.045, 0.044	0.043
CCRMP-SSC-2 Copper rod	~100 Cu	0.0006	0.0005, 0.0005	--
CCRMP-SSC-4 Copper rod	~100 Cu	0.0011	0.0013, 0.0013	--

*NBS provisional result.

†Certified value based on the two results shown in brackets.

#Direct determination of antimony, i.e., without co-precipitation.

Table 4 - Results obtained for arsenic in NBS and BCS copper-base alloys

Sample	Nominal composition, %	Certified value and range, % As	As found, %
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.009	0.0098
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.004	0.0048
NBS-C1118 Aluminum brass A	75.1 Cu, 21.9 Zn, 2.8 Al, 0.1 P	0.007	0.0074
NBS-C1119 Aluminum brass B	77.1 Cu, 20.5 Zn, 2.1 Al, 0.1 P	0.040	0.040
NBS-C1120 Aluminum brass C	80.1 Cu, 18.1 Zn, 1.5 Al, 0.1 Sb	0.090	0.090
NBS-62B Manganese bronze	57.4 Cu, 38.0 Zn, 1.3 Mn, 1.0 Al, 1.0 Sn, 0.8 Fe, 0.3 Pb, 0.3 Ni	0.004	0.0046
NBS-63c Phosphor bronze bearing metal	80.5 Cu, 9.4 Pb, 9.0 Sn, 0.5 Sb, 0.3 Ni, 0.2 P, 0.1 Zn	0.023 (0.017-0.029)	0.023
NBS-124d Ounce metal	83.6 Cu, 5.2 Pb, 5.1 Zn, 4.5 Sn, 1.0 Ni, 0.2 Fe, 0.2 Sb	0.02*	0.015
BCS-Manganese brass "B"	58.8 Cu, 33.9 Zn, 1.0 Mn, 0.9 Fe, 1.6 Al, 1.8 Sn, 0.8 Pb, 1.0 Ni	0.03 (0.02-0.04)†	0.019
BCS-207 Bronze "C"	86.8 Cu, 9.8 Sn, 2.5 Zn, 0.4 Pb	0.05 (0.04-0.07)	0.057
BCS-183/1 Bronze	84.8 Cu, 5.0 Sn, 5.2 Zn, 3.5 Pb, 0.5 P, 0.5 Ni, 0.2 Sb	0.14 (0.12-0.14)	0.127, 0.129

*NBS provisional result.

†Certified value based on four results, viz. 0.03, 0.04, 0.02 and 0.03%.

Table 5 - Results obtained for bismuth in NBS and BCS non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Bi	Bi found, %		
			Spectrophotometric iodide method	Atomic-absorption spectrophotometry	
				DDTC* extraction method	Iron collection method
NBS-C1100 Cartridge brass	67.4 Cu, 32.2 Zn	0.0010	0.0011	0.0011	0.0007
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.0004	0.0004	0.0003	--
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.0005	0.0006	0.0006	--
NBS-53d Lead-base bearing metal	9.9 Sb, 4.9 Sn	0.135 (0.12-0.143)	0.141	0.145	0.140†
NBS-54D Tin-base bearing metal	88.6 Sn, 7.1 Sb, 3.6 Cu, 0.6 Pb	0.044 (0.037-0.050)	0.048	0.050	--
NBS-127A Solder	30.0 Sn, 0.8 Sb	0.036 (0.031-0.04)	0.039	0.035	--
BCS-178 White metal "B"	84.0 Sn, 7.5 Sb, 4.1 Cu, 3.9 Pb	0.005 (0.003-0.008)#	0.0030	0.0038	--
BCS-183/3 Leaded gunmetal	84.5 Cu, 6.7 Sn, 3.3 Zn, 3.4 Pb, 1.5 Ni	0.008 (0.007-0.010)	0.0072	0.0072	0.0068
BCS-207/2 Gunmetal	87.3 Cu, 9.7 Sn, 1.6 Zn, 0.7 Pb	0.04 (0.039-0.048)	0.042	0.045	0.041

*DDTC=diethyldithiocarbamate.

†0.1 g sample taken.

#Certified value based on the two results shown in brackets.

Table 6 - Results obtained for boron in NBS and BCS iron and steel

Sample	Nominal composition, %	Certified value and range, % B	B found, %		
			Acid-soluble	Acid-insoluble	Soluble + insoluble
NBS-3 White iron	2.3 C, 0.4 Mn, 1.0 Si	0.0007 (0.0005-0.0008)*	0.0011_5	NF†	0.0012
			0.0010_3	NF†	0.0010
			0.0010_4	NF†	0.0010
NBS-151 Boron steel	0.6 C, 1.0 Cr, 0.2 Mo	0.0027#	0.0017_8	0.0010_1	0.0028
			0.0018_7	0.0007_5	0.0026
			0.0018_9	0.0007_1	0.0026
BCS-273 Mild steel	0.2 Cu, 0.3 W	0.002_5(0.0015-0.0030)	0.0023_3	0.0001_8	0.0025
			0.0022_4	0.0000_8	0.0023
			0.0021_1	0.0001_6	0.0023
BCS-327 Mild steel	0.2 Mn, 0.2 Cu	0.003 (0.0025-0.0040)	0.0033_2	NF†	0.0033
			0.0033_9	0.0001_4	0.0035
			0.0034_3	0.0000_3	0.0035
BCS-328 Mild steel	0.4 Mn, 0.2 V, 0.2 Co	0.004 (0.0035-0.0050)	0.0044_5	0.0002_9	0.0047
			0.0043_0	0.0004_0	0.0047
			0.0044_0	0.0003_8	0.0048
BCS-329 Mild steel		0.008 (0.0070-0.0080)	0.0078_5	0.0010_3	0.0089
			0.0076_9	0.0014_3	0.0091
			0.0081_3	0.0011_2	0.0093
BCS-330 Mild steel	0.5 Mn	0.007 (0.0070-0.0080)	0.0081_1	0.0000_4	0.0082
			0.0081_6	0.0000_8	0.0082
			0.0081_2	0.0001_8	0.0083

*Certified value based on the two results shown in brackets.

†NF means none found.

#NBS provisional result.

Table 7 - Results obtained for chromium in NBS and BCS iron, steel and non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Cr	Cr found, %
NBS-3 White iron	2.3 C, 0.4 Mn, 1.0 Si, 0.01 Mo, 0.01 V	0.051 (0.049-0.052)	0.052
NBS-5L Cast iron	2.6 C, 0.7 Mn, 0.3 P, 1.8 Si, 1.0 Cu, 0.02 Mo, 0.03 V	0.148 (0.144-0.150)	0.152
NBS-6E Cast iron	2.6 C, 1.4 Mn, 0.4 P, 2.3 Si, 0.3 Cu, 0.02 Mo, 0.02 V	0.074 (0.064-0.082)	0.073
NBS-7f Cast iron	2.8 C, 0.4 Mn, 0.9 P, 1.9 Si, 0.05 V	0.015*	0.013
NBS-10G Bessemer steel	0.2 C, 0.09 Mn	0.008 (0.006-0.01)	0.0076
NBS-19G Acid open-hearth steel	0.2 C, 0.6 Mn, 0.2 Si, 0.01 Mo, 0.01 V	0.374 (0.369-0.380)	0.383, 0.376
NBS-30E Chromium-vanadium steel	0.5 C, 0.8 Mn, 0.3 Si, 0.15 V, 0.01 Mo	0.934 (0.929-0.939)	0.951, 0.949
NBS-36A Chromium-molybdenum steel	0.1 C, 0.4 Mn, 0.4 Si, 0.2 Ni, 0.9 Mo	2.41 (2.39-2.43)	2.42, 2.36†
NBS-55c Open-hearth iron		0.003*	0.0026, 0.0027
NBS-107A Nickel-chromium-molybdenum cast iron	2.7 C, 0.6 Mn, 0.3 P, 1.4 Si, 1.0 Ni, 0.8 Mo, 0.03 V	0.479 (0.469-0.491)	0.494, 0.491
NBS-132 Molybdenum-tungsten-chromium-vanadium steel	0.8 C, 0.3 Mn, 0.2 Si, 1.6 V, 7.1 Mo, 6.3 W	4.11 (4.06-4.14)	4.11, 4.15†
NBS-134A High speed steel	0.8 C, 0.2 Mn, 0.3 Si, 1.3 V, 8.4 Mo, 2.0 W	3.67 (3.64-3.69)	3.71, 3.69†
NBS-153 Molybdenum-cobalt steel	0.5 C, 0.2 Mn, 0.2 Si, 2.0 V, 8.4 Mo, 1.6 W, 8.5 Co	4.14 (4.12-4.17)	4.12, 4.08†
NBS-159 Chromium-molybdenum (silver-bearing) steel	0.5 C, 0.8 Mn, 0.3 Si, 0.05 V, 0.4 Mo, 0.1 Ag	1.00 (0.99-1.03)	1.01, 1.00†
NBS-363 Low-alloy steel	0.6 C, 1.5 Mn, 0.7 Si, 0.3 Ni, 0.3 V, 0.03 Mo, 0.05 W	1.31*	1.32, 1.32†
BCS-273 Mild steel	0.05 Mo, 0.3 W	0.075	0.076
NBS-85A Aluminum alloy	2.5 Cu, 1.6 Mg, 0.7 Mn, 0.4 Ni, 0.2 Fe, 0.1 Si	0.231 (0.226-0.24)	0.233
NBS-86C Aluminum alloy	7.9 Cu, 1.5 Zn, 0.9 Fe, 0.7 Si	0.029 (0.022-0.032)	0.030
NBS-87a Silicon-aluminum alloy	6.2 Si, 0.6 Fe, 0.6 Ni, 0.4 Mg, 0.3 Mn, 0.2 Ti	0.11*	0.121
NBS-162A Nickel-copper alloy	64.0 Ni, 30.6 Cu, 2.2 Fe, 1.6 Mn, 0.9 Si, 0.5 Al	0.042 (0.036-0.048)	0.041
NBS-360 Zircaloy-2	1.4 Sn, 0.2 Fe	0.114*	0.107

*NBS provisional result.

†Results obtained by taking two aliquots of the same sample solution through the extraction step.

Table 8 - Results obtained for cobalt in synthetic nickel, molybdenum and tungsten samples

Matrix	Total Co present, %	Co found, %
Ni*	0.0019	0.0020
	0.0059	0.0060
	0.0109	0.010_8
	0.0259	0.025_9
	0.0509	0.051_1
	0.1009	0.099_7
Mo†	0.0010	0.0010
	0.0050	0.0049
	0.0100	0.0099
	0.0250	0.025_2
	0.0500	0.050_1
W†	0.0010	0.0010
	0.0050	0.0050
	0.0100	0.010_0
	0.0250	0.024_9
	0.0500	0.049_8

*1 g of nickel as nickelous chloride hexahydrate. This compound contained 0.0009% of cobalt calculated on the basis of 1 g of nickel.

†The molybdenum and tungsten metals (1 g) used to prepare the synthetic samples were cobalt-free.

Table 9 - Results obtained for copper in synthetic molybdenum and tungsten samples

Matrix*	Total Cu present, %	Cu found, %
Mo	0.0052	0.0052
	0.0102	0.010_2
	0.0252	0.025_4
	0.0502	0.050_5
	0.1002	0.100_9
W	0.0050	0.0050
	0.0100	0.0098
	0.0250	0.024_9
	0.0500	0.049_9
	0.1000	0.100_1

*The molybdenum and tungsten metals (0.5 g) used to prepare the synthetic solutions contained 0.0002% and no copper, respectively.

Table 10 - Results obtained for iron in synthetic molybdenum and tungsten samples

Matrix*	Total Fe present, %	Fe found, %
Mo	0.0179	0.017_4
	0.0329	0.033_0
	0.0579	0.055_5
	0.1079	0.106_4
W	0.0156	0.016_6
	0.0306	0.031_0
	0.0556	0.056_3
	0.1056	0.107_0

*The molybdenum and tungsten metals (0.5 g) used to prepare the synthetic solutions contained 0.0079 and 0.0056% of iron, respectively.

Table 11 - Results obtained for iron in NBS copper-base alloys

Sample	Nominal composition, %	Certified value, % Fe	Fe found, %
C1103 Free-cutting brass A	35.7 Zn, 3.7 Pb, 0.9 Sn, 0.2 Ni	0.26	0.256, 0.255, 0.261
C1104 Free-cutting brass B	35.3 Zn, 2.8 Pb, 0.4 Sn	0.088	0.090, 0.090, 0.090
C1105 Free-cutting brass C	34.0 Zn, 2.0 Pb, 0.2 Sn	0.044	0.041, 0.041, 0.041
C1106 Naval brass A	40.1 Zn, 0.75 Sn	0.004	0.0041, 0.0042, 0.0041
C1107 Naval brass B	37.3 Zn, 0.2 Pb, 1.0 Sn	0.037	0.038, 0.038
C1108 Naval brass C	34.4 Zn, 0.4 Sn	0.050	0.049, 0.048
C1109 Red brass A	17.4 Zn, 0.1 Sn	0.053	0.054
C1110 Red brass B	15.2 Zn	0.033	0.033
C1111 Red brass C	12.8 Zn	0.010	0.0091
C1112 Gilding metal A	6.3 Zn, 0.1 Sn	0.070	0.068, 0.068, 0.068
C1113 Gilding metal B	4.8 Zn	0.043	0.040, 0.039, 0.039
C1114 Gilding metal C	3.5 Zn	0.017	0.016, 0.016, 0.016
C1115 Commercial bronze A	11.7 Zn, 0.1 Sn	0.13	0.126, 0.126, 0.128
C1116 Commercial bronze B	9.4 Zn	0.046	0.044, 0.044, 0.045
C1117 Commercial bronze C	6.9 Zn	0.014	0.014, 0.014, 0.014
C1118 Aluminum brass A	21.9 Zn, 2.8 Al	0.065	0.065, 0.065, 0.066
C1119 Aluminum brass B	20.5 Zn, 2.1 Al	0.030	0.030, 0.030, 0.029
C1120 Aluminum brass C	18.1 Zn, 0.1 Pb, 1.5 Al, 0.1 Sb	0.015	0.014, 0.015, 0.014
124d Ounce metal	5.1 Zn, 5.2 Pb, 4.6 Sn, 0.2 Sb, 1.0 Ni	0.18	0.181

Table 12 - Results obtained for manganese in synthetic molybdenum and tungsten samples

Matrix*	Total Mn present, %	Mn found, %
Mo	0.0013	0.0013
	0.0053	0.0052
	0.0103	0.010_3
	0.0253	0.025_3
	0.0503	0.050_7
	0.1003	0.101_7
W	0.0010	0.0009
	0.0050	0.0049
	0.0100	0.010_0
	0.0250	0.024_8
	0.0500	0.049_7
	0.1000	0.098_8

*The molybdenum and tungsten metals (0.5 g) used to prepare the synthetic solutions contained 0.0003 and no manganese, respectively.

Table 13 - Results obtained for molybdenum in NBS and BCS iron and steel

Sample	Nominal composition, %	Certified value and range, % Mo	Mo found, %	
			After α-benzoinoxime extraction	After α-benzoinoxime and xanthate extractions
NBS-3b White iron	0.4 Mn, 1.0 Si, 2.4 C	0.002 (0.001-<0.01)	0.0015, 0.0014	--
NBS-4j Cast iron	3.0 C, 0.8 Mn, 1.3 Si	0.080*	0.078	--
NBS-12H Basic open-hearth steel	0.8 Mn, 0.2 Si	0.006 (0.005-0.007)	0.0050, 0.0048	--
NBS-33d Nickel steel	3.6 Ni, 0.5 Mn, 0.3 Si	0.246 (0.242-0.249)	0.245	--
NBS-36A Chromium-molybdenum steel	0.4 Si, 2.4 Cr, 0.4 Mn	0.920 (0.91-0.930)	0.918	--
NBS-50a Chromium-tungsten-vanadium steel	18.3 W, 3.5 Cr, 1.0 V, 0.5 Si, 0.7 Cu	0.009 (0.005-0.014)	--	0.016, 0.016
NBS-50B Tungsten-chromium-vanadium steel	18.1 W, 0.7 C, 0.3 Si, 4.1 Cr, 1.0 V	0.401 (0.384-0.415)	--	0.401
NBS-111a Nickel-molybdenum steel	0.7 Mn, 0.3 Si, 1.7 Ni	0.222*	0.227	--
NBS-121B 18 Chromium-11 nickel steel	1.5 Mn, 0.6 Si, 11.2 Ni, 17.7 Cr, 0.4 Ti	0.073 (0.070-0.076)	0.073	--
NBS-123b Niobium-tantalum stabilized stainless steel	0.2 W, 0.8 Nb, 0.2 Ta, 0.5 Si	0.17*	0.166	0.172
NBS-152 Open-hearth steel	0.5 C, 0.8 Mn, 0.2 Si	0.013*	0.013	--
NBS-155 Chromium-tungsten steel	0.5 W, 1.2 Mn, 0.3 Si, 0.5 Cr, 0.9 C	0.039 (0.035-0.043)	0.037	0.038
NBS-160A 19 Chromium-14 nickel-3 molybdenum steel	14.1 Ni, 18.8 Cr, 1.6 Mn, 0.6 Si	2.83*	2.84	--
BCS-219/2 Nickel-chromium molybdenum steel	0.2 W, 2.5 Ni, 0.8 Cr, 0.3 Si, 0.6 Mn	0.43 (0.41-0.45)	0.427	0.425
BCS-273 Mild steel	0.3 W	0.04_5	0.041	0.040

*NBS provisional result.

Table 14 - Results obtained for nickel in synthetic molybdenum and tungsten samples

Matrix*	Total Ni present, %	Ni found, %
Mo	0.0011	0.0012
	0.0051	0.0052
	0.0101	0.010_1
	0.0251	0.024_8
	0.0501	0.050_1
	0.0901	0.090_4
W	0.0018	0.0018
	0.0058	0.0058
	0.0108	0.010_8
	0.0258	0.025_8
	0.0508	0.050_9
	0.0908	0.090_5

*The molybdenum and tungsten metals (0.5 g) used to prepare the synthetic solutions contained 0.0001 and 0.0008% of nickel, respectively.

Table 15 - Results obtained for nickel in NBS and BCS copper-base alloys

Sample	Nominal composition, %	Certified value and range, % Ni	Ni found, %*
NBS-C1101 Cartridge brass B	30.3 Zn	0.013 (0.013-0.014)	0.014, 0.014, 0.014
NBS-C1102 Cartridge brass C	27.1 Zn	0.005 (0.005-0.006)	0.005, 0.005, 0.005
NBS-C1103 Free-cutting brass A	35.7 Zn, 3.7 Pb, 0.9 Sn	0.16	0.151, 0.151, 0.150
NBS-C1104 Free-cutting brass B	35.3 Zn, 2.8 Pb, 0.4 Sn	0.070	0.070, 0.070, 0.071
NBS-C1105 Free-cutting brass C	34.0 Zn, 2.0 Pb, 0.2 Sn	0.043	0.044, 0.045, 0.045
NBS-C1106 Naval brass A	40.1 Zn, 0.7 Sn	0.025 (0.024-0.025)	0.025, 0.025, 0.025
NBS-C1107 Naval brass B	37.3 Zn, 1.0 Sn	0.098	0.098, 0.098, 0.098
NBS-C1108 Naval brass C	34.4 Zn, 0.4 Sn	0.033 (0.031-0.037)	0.032, 0.032, 0.032
NBS-C1109 Red brass A	17.4 Zn	0.10 (0.10-0.12)	0.104, 0.103, 0.104
NBS-C1110 Red brass B	15.2 Zn	0.053 (0.051-0.054)	0.052, 0.052, 0.052

(Table 15 cont'd)

Sample	Nominal composition, %	Certified value and range, % Ni	Ni found, %*
NBS-C1111 Red brass C	12.8 Zn	0.022	0.021, 0.021, 0.021
NBS-C1112 Gilding metal A	6.3 Zn	0.100	0.099, 0.098, 0.097
NBS-C1113 Gilding metal B	4.8 Zn	0.057	0.056, 0.056, 0.056
NBS-C1114 Gilding metal C	3.5 Zn	0.021	0.021, 0.021, 0.021
NBS-C1115 Commercial bronze A	11.7 Zn	0.074	0.073, 0.074, 0.074
NBS-C1116 Commercial bronze B	9.4 Zn	0.048	0.048, 0.048, 0.047
NBS-C1117 Commercial bronze C	6.9 Zn	0.020	0.020, 0.020, 0.020
NBS-37E Sheet brass	27.9 Zn, 1.0 Pb, 1.0 Sn	0.53 (0.52-0.55)	0.534
NBS-52c Cast bronze	2.1 Zn, 7.9 Sn	0.76 (0.76-0.77)	0.759
NBS-62D Manganese bronze	37.1 Zn, 1.2 Al, 0.7 Mn	0.28 (0.27-0.29)	0.286
NBS-63C Phosphor bronze bearing metal	9.4 Pb, 9.0 Sn, 0.5 Sb, 0.1 P	0.32 (0.31-0.32)	0.312
NBS-124d Ounce metal	5.1 Zn, 5.2 Pb, 4.6 Sn	0.99	0.998
NNBS-158 Silicon bronze	2.1 Zn, 2.7 Si, 1.5 Fe, 1.3 Mn, 1.0 Sn, 0.5 Al	0.006 (0.0056-0.0064)	0.0063
NBS-164 Manganese aluminum bronze	21.9 Zn, 2.5 Fe, 4.7 Mn, 0.6 Sn, 6.2 Al	0.046 (0.044-0.05)	0.046
NBS-184 Leaded tin bronze	2.7 Zn, 1.4 Pb, 6.4 Sn	0.50 (0.48-0.51)	0.509
BCS-183/1 Bronze	5.2 Zn, 3.5 Pb, 5.0 Sn, 0.5 P, 0.2 Sb, 0.1 As	0.51 (0.47-0.53)	0.503
BCS-207 Bronze "C"	2.5 Zn, 9.8 Sn	0.09 (0.08-0.11)	0.095
BCS-179 Manganese brass "B"	33.9 Zn, 0.8 Pb, 1.8 Sn, 0.9 Fe, 1.0 Mn, 1.6 Al	1.01 (0.96-1.05)	1.00

*Results for NBS "C" series alloys taken from the following reports:

-LaRochelle, A.E., Penner (Donaldson), E.M., McMaster, C.H. and Inman, W.R. "Determination of copper, zinc, iron, nickel, tin and lead in spectrographic standard samples of brasses for the National Bureau of Standards, Washington, D.C."; Mineral Sciences Division Test Report AC-62-18; Mines Branch, Energy, Mines and Resources Canada; 1962.

-Idem. "Analysis of brasses, bronzes and gilding metal for the National Bureau of Standards, Washington, D.C."; Mineral Sciences Division Test Report AC-63-92; Mines Branch, Energy, Mines and Resources Canada; 1963.

Table 16 - Results obtained for nickel in NBS and BCS magnesium- and aluminum-base alloys

Sample	Nominal composition, %	Certified value and range, % Ni	Ni found, %
NBS-171 Magnesium-base alloy	3.0 Al, 1.0 Zn, 0.5 Mn	0.0009 (0.0007-0.0014)	0.0008
NBS-85B Aluminum alloy	4.0 Cu, 0.6 Mn, 0.2 Si	0.084 (0.079-0.091)	0.089, 0.088
NBS-86C Aluminum alloy	7.9 Cu, 0.7 Si	0.030 (0.02-0.035)	0.030, 0.030
NBS-87a Silicon aluminum alloy	6.2 Si, 0.3 Mn	0.57	0.561
BCS-182/1 Silicon aluminum alloy	11.5 Si, 0.3 Mn	0.04 (0.03-0.05)	0.040
BCS-268 Silicon aluminum alloy	4.9 Si, 1.3 Cu, 0.2 Mn	0.12 (0.11-0.136)	0.120
BCS-307 Cerium zinc zirconium magnesium alloy	2.8 rare-earth elements, 2.1 Zn, 0.6 Zr	0.001 or less	0.0006
NBS-171		0.0109*	0.010_9
BCS-307		0.0106†	0.010_5

*0.01% nickel added.

†Value includes nickel found and 0.01% added.

Table 17 - Results obtained for selenium in CCRMP commercial-purity copper rods

Sample	Recommended value, µg/g Se	Se found, µg/g
SSC-1	7.3	8.8, 9.0
SSC-2	2.6	2.8, 3.4
SSC-3	3.9	4.8, 5.0
SSC-4	2.9	3.4, 3.6

Table 18 - Results obtained for silicon in synthetic copper-base alloys

Sample	Total Si present, %	Si found, %
Cu metal*	0.0014	0.0014
	0.0044	0.0043
	0.0084	0.0085
C1118 Aluminum brass A†	0.0031	0.0033
	0.0051	0.0052
	0.0081	0.0078

*The copper metal (1 g) used to prepare the synthetic solutions contained 0.0004% of silicon.

†Si present, 0.0021% (see Table 19).

Table 19 - Results obtained for silicon in NBS copper-base alloys

Sample	Nominal composition, %	Certified value, % Si	Si found, %*
C1100 Cartridge brass	0.1 Pb, 0.01 P	0.01†	0.0094, 0.0095, 0.0094
C1101 Cartridge brass B	0.002 P, 0.009 As	0.005†	0.0050, 0.0048, 0.0050
C1102 Cartridge brass C	0.005 P, 0.004 As	0.002†	0.0017, 0.0018, 0.0015
C1118 Aluminum brass A	2.8 Al, 0.13 P, 0.007 As	0.0021	0.0021, 0.0020, 0.0023
C1119 Aluminum brass B	2.1 Al, 0.07 P, 0.04 As	0.0015	0.0015, 0.0015, 0.0015
C1120 Aluminum brass C	1.5 Al, 0.018 P, 0.09 As	0.0011	0.0013, 0.0011, 0.0009

*Results taken from the following reports:

-Penner (Donaldson), E.M. and Inman, W.R. "Determination of silicon in aluminum brasses for NBS spectrographic standards"; Mineral Sciences Division Test Report AC-64-51; Mines Branch, Energy, Mines and Resources Canada; 1964.

-LaRochelle, A.E., Penner (Donaldson), E.M., McMaster, C.H. and Inman, W.R. "Determination of arsenic, beryllium, bismuth, cadmium, manganese, phosphorus and silicon in spectrographic standard samples of brasses for the National Bureau of Standards, Washington, D.C."; Mineral Sciences Division Test Report AC-64-138; Mines Branch, Energy, Mines and Resources Canada; 1964.

†Value given for information only; not certified.

Table 20 - Results obtained for tellurium in NBS copper-base alloys

Sample	Certified value, µg/g Te	Te found, µg/g
C1100 Cartridge brass	35	34.8, 34.3
C1101 Cartridge brass B	15	13.5, 13.4
C1102 Cartridge brass C	3	0.8, 0.8

Table 21 - Results obtained for tin in NBS and BCS iron, steel and non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Sn	Sn found, %	
			Atomic-absorption spectrophotometry	Spectrophotometric gallein method
NBS-19G Acid open-hearth steel	0.6 Mn, 0.2 Si, 0.4 Cr, 0.03 Nb	0.008 (0.008-0.009)	0.0081	0.0095
NBS-32E Nickel-chromium steel	0.8 Mn, 0.3 Si, 1.2 Ni, 0.7 Cr	0.011*	0.011, 0.011	0.013
NBS-33C Nickel steel	0.7 Mn, 0.3 Si, 3.3 Ni	0.003 (0.003-0.004)	0.0025	--
NBS-36A Chromium-molybdenum steel	0.4 Mn, 0.4 Si, 2.4 Cr, 0.9 Mo	0.011 (0.010-0.012)	0.010	0.012
NBS-55e Open-hearth iron	0.01 As	0.007 (0.006-0.008)	0.0054, 0.0054	--
NBS-101E 18 chromium-9 nickel steel	1.8 Mn, 0.4 Si, 9.5 Ni, 18.0 Cr, 0.4 Mo	0.020 (0.019-0.023)	0.020	--
NBS-125 High silicon steel	5.0 Si	0.007 (0.005-0.008)	0.0066	0.0092
NBS-152 Basic open-hearth steel	0.8 Mn, 0.2 Si	0.036 (0.035-0.039)	0.037	--
NBS-160A 19 Chromium-14 nickel-3 molybdenum steel	1.6 Mn, 0.6 Si, 14.1 Ni, 18.7 Cr, 2.8 Mo	0.013 (0.010-0.017)	0.012	--
BCS-218/2 Carbon steel	0.6 Mn, 0.2 Si, 0.04 As	0.035 (0.032-0.037)	0.033, 0.033	0.034
BCS-273 Mild steel		0.065 (0.060-0.068)	0.065	0.065
NBS-37E Sheet brass	69.6 Cu, 27.9 Zn, 1.0 Pb	1.00 (0.98-1.02)	0.995	1.02
NBS-62D Manganese bronze	59.1 Cu, 37.1 Zn, 1.2 Al, 0.7 Mn	0.38 (0.37-0.40)	0.397	0.403
NBS-157A Copper-nickel-zinc alloy	58.6 Cu, 29.1 Zn, 11.8 Ni	0.021 (0.016-0.026)	0.022	0.024
NBS-158 Silicon bronze	90.9 Cu, 2.7 Si, 2.1 Zn, 1.3 Mn	0.97 (0.96-0.99)	0.990	0.985
NBS-164 Manganese-aluminum bronze	63.8 Cu, 21.9 Zn, 6.2 Al, 4.7 Mn	0.63 (0.60-0.64)	0.632	0.673, 0.655
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.016	--	0.017
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.006	--	0.0058
NBS-C1116 Commercial bronze B	90.4 Cu, 9.4 Zn	0.044	--	0.043
BCS-Manganese brass "B"	58.8 Cu, 33.9 Zn, 1.0 Mn, 0.9 Fe, 1.6 Al, 1.0 Ni, 0.05 Sb	1.75 (1.64-1.88)	--	1.74
NBS-94B Zinc-base alloy	4.1 Al	0.006 (0.005-0.006)	0.0055	0.0056
NBS-87 Silicon-aluminum alloy	6.2 Si, 0.6 Ni, 0.2 Ti	0.063 (0.05-0.077)	0.063	0.063
BCS-268 Silicon-aluminum alloy	4.9 Si, 1.3 Cu	0.03	0.031	0.029
NBS-176 Titanium-base alloy	5.2 Al	2.47*	2.49	--
NBS-360 Zircaloy-2		1.43*	1.45	1.44

*NBS provisional result.

Table 22 - Results obtained for titanium in synthetic molybdenum, tungsten and aluminum samples

Matrix*	Total Ti present, %	Ti found, %†
Mo	0.0013	0.0012
	0.0053	0.0050
	0.0103	0.010_3
	0.0253	0.025_3
	0.0503	0.049_9
	0.1003	0.100_3
W	0.0010	0.0009
	0.0050	0.0050
	0.0100	0.010_0
	0.0250	0.025_0
	0.0500	0.049_9
	0.1000	0.100_1
Al	0.0011	0.0011
	0.0051	0.0052
	0.0101	0.010_6
	0.0251	0.025_0
	0.0501	0.050_5

*The molybdenum, tungsten and aluminum metals (0.5 g) used to prepare the synthetic samples contained 0.0003, none, and 0.0001% of titanium, respectively.

†The results for the aluminum samples are taken from reference 2 (p 97).

Table 23 - Results obtained for titanium in NBS and BCS iron, steel and non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Ti	Ti found, %*
NBS-85B Aluminum alloy	4.0 Cu, 0.2 Fe, 0.6 Mn, 0.2 Si, 1.5 Mg, 0.2 Cr	0.022 (0.022-0.024)	0.022
NBS-86C Aluminum alloy	7.9 Cu, 1.5 Zn, 0.9 Fe, 0.7 Si	0.035 (0.033-0.036)	0.035
BCS-263 Aluminum alloy	0.4 Fe, 0.5 Mn, 0.2 Si, 4.2 Mg, 0.3 Cr	0.05 (0.045-0.056)	0.052
BCS-268 Silicon-aluminum alloy	1.4 Cu, 0.6 Mg, 4.9 Si, 0.4 Fe, 0.2 Mn	<0.02 (0.01-0.02)	0.014
NBS-162A Nickel-copper alloy	30.6 Cu, 64.0 Ni, 2.2 Fe, 1.6 Mn, 0.5 Al, 0.9 Si	0.005 (0.004-0.007)	0.0044
NBS-169 Nickel-chromium alloy	77.3 Ni, 20.3 Cr, 1.4 Si, 0.5 Fe, 0.2 Co	0.006 (0.005-0.009)	0.0056
NBS-4i Cast iron	3.3 C, 0.8 Mn, 1.5 Si, 0.3 Cu	0.026 (0.022-0.029)	0.027
NBS-6F Cast iron	2.9 C, 0.5 Mn, 0.5 P, 1.9 Si, 0.3 Cu, 0.4 Cr	0.063 (0.055-0.070)	0.059
NBS-115 Copper-nickel-chromium cast iron	2.4 C, 1.0 Mn, 1.6 Si, 6.4 Cu, 15.9 Ni, 2.2 Cr	0.021	0.028
NBS-121b Chromium-nickel steel	1.5 Mn, 0.6 Si, 11.1 Ni, 17.7 Cr	0.414 (0.410-0.419)	0.399
NBS-122d Cast iron	3.3 C, 0.5 Mn, 0.3 P, 0.6 Si	0.007 (0.005-0.009)	0.0054

*Results taken from reference 2 (p 97).

Table 24 - Results obtained for tungsten in NBS and BCS steel

Sample	Nominal composition, %	Mo, %	Certified value and range, % W	W found, %
NBS-50a Chromium-tungsten steel	0.3 Mn, 0.5 Si, 3.5 Cr, 1.0 V, 0.1 Cu, 0.1 Ni, 0.04 As	0.009	18.25 (18.16-18.34)	18.2
NBS-50B Tungsten-chromium-vanadium steel	0.3 Mn, 0.3 Si, 0.1 Cu, 0.1 Ni, 4.1 Cr, 1.0 V, 0.04 As	0.401	18.05 (17.95-18.14)	17.9
NBS-101E Chromium-nickel steel	1.8 Mn, 0.4 Si, 0.4 Cu, 9.5 Ni, 18.0 Cr, 0.04 V, 0.2 Co	0.426	0.056	0.054†
NBS-123a Chromium-nickel steel (niobium-bearing)	0.8 Nb, 0.04 V, 0.5 Si, 18.1 Cr	0.12	0.11*	0.108
NBS-123b Niobium-tantalum stabilized stainless steel	0.8 Nb, 0.2 Ta, 0.5 Si, 0.05 V	0.17	0.18*	0.182
NBS-134A Molybdenum-tungsten high-speed steel	0.2 Mn, 0.3 Si, 0.1 Cu, 0.1 Ni, 3.7 Cr, 1.3 V	8.35	2.00 (1.97-2.05)	2.03†
NBS-153 Cobalt-molybdenum-tungsten steel	0.2 Mn, 0.2 Si, 0.1 Cu, 0.1 Ni, 4.1 Cr, 2.0 V, 8.5 Co	8.38	1.58 (1.54-1.61)	1.55†
NBS-155 Chromium-tungsten steel	1.2 Mn, 0.3 Si, 0.1 Cu, 0.1 Ni, 0.5 Cr, 0.02 V	0.039	0.517 (0.508-0.526)	0.517
BCS-220/1 Tungsten-molybdenum high-speed steel	5.1 Cr, 2.1 V, 0.1 Co, 0.2 Si, 0.3 Mn, 0.2 Ni, 0.2 Cu, 0.03 As	5.20	6.86 (6.78-7.00)	6.78
BCS-246 Niobium-molybdenum 18/12 stainless steel	0.8 Nb, 18.8 Cr, 12.1 Ni, 0.1 Cu	2.89	0.22 (0.19-0.23)	0.223†
BCS-271 Mild steel	0.1 Cr, 0.1 Sn	0.19	0.01_5 (0.013-0.019)	0.016
BCS-273 Mild steel	0.1 Cr, 0.2 Cu, 0.1 Sn, 0.05 V	0.045	0.28_0 (0.271-0.282)	0.287
BCS-281 Low-tungsten steel	0.1 Si, 0.1 Mn	0.02	0.70 (0.68-0.73)	0.696
BCS-282 Low-tungsten steel	0.1 Si, 0.1 Mn, 0.1 Cr, 0.02 V	0.02	1.30 (1.28-1.32)	1.29

*NBS provisional result.

†Molybdenum removed by xanthate-chloroform extraction.

Table 25 - Results obtained for vanadium in NBS iron, steel and non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, %V	V found, %
6F Cast iron	0.4 Cr, 0.1 Ti, 0.5 Mn	0.032 (0.027-0.038)	0.031
19G Acid open-hearth steel	0.4 Cr, 0.6 Mn	0.012	0.012
30E Chromium-vanadium steel	0.9 Cr, 0.8 Mn	0.149 (0.146-0.152)	0.146
32E Nickel-chromium steel	0.7 Cr, 1.2 Ni, 0.8 Mn	0.002 (0.001-0.004)	0.0013
36A Chromium-molybdenum steel	2.4 Cr, 0.9 Mo, 0.4 Mn	0.006 (0.005-0.007)	0.0041, 0.0040*
85B Aluminum alloy	0.2 Cr, 4.0 Cu, 1.5 Mg, 0.6 Mn	0.006	0.0069
87A Silicon-aluminum alloy	6.2 Si, 0.2 Ti, 0.1 Cr	<0.01	0.0080
100A Manganese steel	1.7 Mn	0.003	0.0019
101E Chromium-nickel steel	18.0 Cr, 9.5 Ni, 1.8 Mn	0.043 (0.038-0.045)	0.039*, 0.039*
106B Chromium-molybdenum-aluminum steel	1.2 Cr, 0.2 Mo, 1.1 Al, 0.5 Mn	0.003 (0.002-0.005)	0.0030
111A Nickel-molybdenum steel	1.7 Ni, 0.2 Mo, 0.2 Cr, 0.7 Mn	0.002	0.0020
133 Chromium-molybdenum steel	13.6 Cr, 0.6 Mo, 0.8 Mn	0.020 (0.014-0.025)	0.018*
139 Chromium-nickel-molybdenum steel	0.5 Cr, 0.6 Ni, 0.2 Mo, 0.9 Mn	0.002	0.0016
155 Chromium-tungsten steel	0.5 Cr, 0.5 W, 1.2 Mn	0.014 (0.010-0.022)	0.012
159 Chromium-molybdenum-silver steel	1.0 Cr, 0.4 Mo, 0.1 Ag, 0.8 Mn	0.054 (0.046-0.06)	0.053
160A Chromium-nickel-molybdenum steel	18.8 Cr, 14.1 Ni. 2.8 Mo, 1.6 Mn	0.052	0.050*
161 Nickel-chromium casting alloy	64.3 Ni, 16.9 Cr, 15.0 Fe, 0.5 Co, 1.3 Mn	0.029 (0.023-0.034)	0.029*

*Mercury cathode separation of chromium.

Table 26 - Results obtained for zinc in synthetic nickel, molybdenum and tungsten samples

Matrix	Total Zn present, %	Zn found, %
Ni*	0.0022	0.0026
	0.0062	0.0060
	0.0112	0.010_7
	0.0262	0.025_9
	0.0512	0.051_4
	0.1012	0.101_1
Mo†	0.0012	0.0011
	0.0052	0.0051
	0.0102	0.010_1
	0.0252	0.025_3
	0.0502	0.050_2
W†	0.0011	0.0010
	0.0051	0.0049
	0.0101	0.010_0
	0.0251	0.024_8
	0.0501	0.050_1

*1 g of nickel added as nickelous chloride hexahydrate. This compound contained 0.0012% of zinc calculated on the basis of 1 g of nickel.

†The molybdenum and tungsten metals (1 g) used to prepare the synthetic solutions contained 0.0002 and 0.0001% of zinc, respectively.

APPENDIX B

Table 1 - Common acids and alkalies - useful data

	HCl	HNO_3	HF	$HClO_4$	H_2SO_4	H_3PO_4	CH_3COOH	NH_4OH
Molecular mass	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
Grams of "active" ingredient per mL	0.426	0.985	0.552	1.19	1.77	1.44	1.055	0.527
Molarity of concentrated reagent	11.7	15.6	27.6	11.8	18.0	14.7	17.6	15.1
Volume (mL) of concentrated reagent per litre of 1 M solution	85.5	64.0	36.2	84.4	55.6	68.2	56.9	66.5