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CANADA

**DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA**

**MINES BRANCH
TECHNICAL BULLETIN**

TB 24

Price 25 cents.

**FLAME PHOTOMETRIC
METHODS USED IN THE
MINERAL SCIENCES DIVISION,
MINES BRANCH, OTTAWA**

ELSIE M. PENNER AND W. R. INMAN

MINERAL SCIENCES DIVISION

**CANMET INFORMATION CENTRE
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SEPTEMBER 1961

ERRATA

TECHNICAL BULLETIN TB 24

Page 5 - Para 2 - Line 2 change powder to power

Page 21 - Note - Line 2 delete iron

Page 28 - Under Determination of Li: Line 8 insert
with, 20, 10, 5.....

Mines Branch Technical Bulletin TB 24

FLAME PHOTOMETRIC METHODS USED
IN THE MINERAL SCIENCES DIVISION,
MINES BRANCH, OTTAWA

by

Elsie M. Penner* and W.R. Inman**

- - -

ABSTRACT

Flame photometric methods are described for the determination of sodium, potassium, lithium and calcium in a variety of materials, including rocks, minerals, ores, metals, alloys, and ceramic materials.

Most of these methods have been developed in the Analytical Chemistry Subdivision of the Mineral Sciences Division, Mines Branch. Some are modifications of existing methods.

Procedures are given regarding decomposition of samples, elimination of interferences, and operation of the Perkin-Elmer flame photometer.

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Direction des mines

Bulletin technique TB 24

PROCÉDÉS PHOTOMÉTRIQUES À FLAMME EN USAGE
À LA DIVISION DES SCIENCES MINÉRALES,
DIRECTION DES MINES, OTTAWA

par

Elsie M. Penner* et W.R. Inman**

RÉSUMÉ

Le présent bulletin décrit les procédés photométriques à flamme qui servent au dosage du sodium, du potassium, du lithium et du calcium dans divers matériaux, notamment les roches, les minéraux, les minerais, les métaux, les alliages et les matières céramiques.

La plupart de ces procédés ont été mis au point à la subdivision même de la chimie analytique, Division des mines. Certains d'entre eux constituent des variantes de procédés déjà existants.

Le présent bulletin décrit, en plus, certain procédés relatifs à la décomposition des échantillons, à l'élimination des interférences et au fonctionnement du photomètre à flamme Perkin-Elmer.

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1. INTRODUCTION

The flame photometer is an emission spectrometer combining a flame source and a photoelectric detection system for the measurement of light intensity. It is designed to measure quantitatively the light emitted by certain metals--i.e. alkali and alkaline earth metals--when they are atomized from solution, led to a burner, and excited to spectral emission in a flame. The intensity of the light emitted by each element is proportional to the concentration of its atoms in the flame at any given instant.

In practice, flame photometry is not quite as simple as the above statement implies. Accurate measurement of the light intensity produced by a given element must take into consideration "interference effects". This term, in flame photometry, refers to the effect of foreign elements or materials in solution--i.e. acids, bases, salts, and metallic ions--on the emission of the element to be analyzed. This effect can be one of enhancement, or suppression, of the desired element when compared with the same concentration in a standard that does not contain the other materials. Interference effects that are directly related to the composition of the solution are those caused by weak emission lines and molecular band emissions of the interfering elements which fall in the analytical wave length range. Physical effects related to composition are differences in surface tension and viscosity, which in turn can produce changes

in rate of atomization, in portion of sample nebulized, and in flame characteristics. This has been explained ^{(1)*} as being due to differences in the rate of evaporation from the mist droplets which occurs in the spray chamber; in other words, the presence of acids or salts in the mist droplets is said to hinder evaporation of the droplets and the resulting increased amount of water carried into the flame reduces the radiation intensity produced in the flame by the test element.

There are three ways of compensating for or eliminating the interferences caused by large amounts of foreign ions in solution, namely:

- (a) Synthetic standards method, ⁽²⁾ i.e. the addition of equivalent amounts of the interfering ions to the standards to compensate for those present in the sample. The drawback to this method is that it requires preliminary knowledge of the composition of the sample, preparation of separate standards for each sample, and the use of extremely pure reagents in order that addition of the requisite amounts of interfering ions to the standard solutions shall not introduce appreciable amounts of the element being determined.

*References are listed at the end of the report in the order in which they are numbered in the text.

- (b) Radiation buffer method, ⁽³⁾ i.e. addition of high concentrations of interfering ions to both the comparison standards and the sample in order to minimize the effects of viscosity changes and of small concentration variations of the interfering ions within the sample under investigation. In using this method care must be taken that the total dissolved salt concentration is not too high, or solid salt may collect on parts of the burner.
- (c) Chemical separation method, i.e. removal of foreign ions by chemical means, e.g. solvent extraction, volatilization, mercury cathode separation, hydrolysis, etc. This is by far the best method.

Two methods ⁽⁴⁾ may be used for measuring the light intensity produced by a given element, the direct intensity method and the internal standard method. The direct intensity method is the simplest approach to flame photometry; in it the sample is introduced into the flame, the amount of light emitted by the desired element is measured, and the photometer reading is related to the concentration. In the internal standard method, however, a known amount of an element (the Perkin-Elmer instruction manual ⁽⁴⁾ suggests lithium) is added to both the sample and the standards, and measurement is then made of the ratio of the intensity of the

unknown element, which is measured on one phototube, to that of the known internal standard lithium, which is measured on another.

It is generally assumed that the internal standard method is more accurate than the direct intensity method, since the direct method assumes that sample viscosity, rate of atomization, flame temperature, and gas and air pressures remain constant. Changes in any of these variables would result in some error in reading. In the case of the internal standard method, these physical variables would tend to affect the light emitted by the internal standard lithium and that emitted by either sodium or potassium in the same way, and therefore the ratio of lights emitted would tend to be the same. However, the presence of large amounts of foreign ions in solution will not necessarily affect both the internal standard lithium and the sodium or potassium in the same way, and therefore the ratio of emitted lights will either increase or decrease, depending on whether the foreign ions have a greater effect on the lithium or on the element being determined. Error can also result from the presence of small amounts of lithium in the samples, e.g. rock samples. Therefore, the assumption that the internal standard method is more accurate is not always strictly true. With proper control of gas and air pressures, and compensation for or elimination of interfering ions, the direct intensity method is just as accurate as, and in some cases

more so than, the internal standard method, and it is also considerably simpler.

The methods described in this bulletin, for the determination of sodium, potassium, lithium and calcium in various materials, have all been used extensively in the chemistry section of the Mineral Sciences Division of the Mines Branch. They either have been developed there or are modifications of published methods. They all utilize the Perkin-Elmer Model 146 flame photometer and the direct intensity method of measurement.

2. APPARATUS

Perkin-Elmer Flame Photometer, Model 146

The instrument requires a nominal 115 volt, 60 cps, ac powder supply, and draws approximately 50 watts. A Raytheon voltage stabilizer provides a separate line to the main power in order to reduce line variation.

A supply of clean compressed air at a constant pressure is essential. A Fisher Governor Pressure Regulator is supplied with the instrument and comes equipped with a Taylor Air Filter. Installation should be from mains to air filter to regulator to instrument. The line pressure should be between 30 to 150 psi or sufficient to maintain a constant 10-pound pressure to the atomizer after being reduced by the air-regulating valve provided.

Tank propane and acetylene gas are used as fuel, and the tanks are each equipped with a double-stage regulator to which a single-stage regulator is connected. Gas pressure is reduced from tank pressure to 5 psi to 1 psi before being admitted to the instrument. A pressure regulator which automatically maintains a constant fuel pressure at approximately 1 psi is built into the instrument.

Eberbach Dyna-Cath Mercury Cathode

Leeds and Northrup pH Meter, Cat. No. 7664

3. INSTRUMENT OPERATION

Propane gas is used for sodium and potassium determinations and acetylene gas for lithium and calcium. Instrument zero is set with distilled water. Sample radiation intensity readings are taken and converted to concentration by comparison between suitable standards giving intensities a little higher and lower than the solution in question, i.e. reading between a low and a high standard. All readings except very low ones (i.e. less than 1 ppm of Na, K, or Li, and less than 5 ppm of Ca) are made using the centre portion of the scale (i.e. approx. 30 to 60). Sample readings are determined as an average of three or more scale readings.

4. PREPARATION OF STANDARD SOLUTIONS

Standard Lithium Solution - 1000 ppm Li

Weigh 4.6095 g of lithium sulphate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) into a 250-ml beaker. Dissolve in distilled water and make to 500 ml. Store in a polyethylene bottle.

Standard Sodium Solution - 1000 ppm Na

Weigh 1.2709 g of sodium chloride (NaCl dried at 125°C) into a 250-ml beaker. Dissolve in distilled water and make to 500 ml. Store in a polyethylene bottle.

Standard Potassium Solution - 1000 ppm K

Weigh 0.9534 g of potassium chloride (KCl dried at 125°C) into a 250-ml beaker. Dissolve in distilled water and make to 500 ml. Store in a polyethylene bottle.

Standard Sodium + Potassium Solution - 1000 ppm(Na + K)

Weigh 1.2709 g of dried NaCl and 0.9534 g of dried KCl into a 250-ml beaker. Dissolve in distilled water and make to 500 ml. Store in a polyethylene bottle.

Standard Calcium Solution - 1000 ppm Ca

Weigh 1.2486 g of low alkali C.P. calcium carbonate (CaCO_3) into a 400-ml beaker. Add approximately 100 ml distilled water. Cover with a watch glass and dissolve by the slow addition of 1.6 ml of concentrated nitric acid (HNO_3). Cool, make to 500 ml, and store in a polyethylene bottle.

Prepare 100-ppm solutions of each of the above by diluting 50 ml of each to 500 ml. Store in polyethylene bottles.

5. REAGENTS

For Determination of Sodium and Potassium

Radiation Buffer Solution

Weigh 86.9 g of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Baker and Adamson low in alkali) and 22.6 g of ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) into a 600-ml beaker. Dissolve in approximately 150 ml of distilled water. Weigh 7.80 g of calcium carbonate (CaCO_3 C.P. low in alkali) and 3.13 g of pure magnesium metal into a 600-ml beaker. Add approximately 200 ml distilled water, cover, and add slowly 40 ml concentrated HCl. Filter both solutions into a 500-ml volumetric flask, make to volume, and store in a polyethylene bottle. (10 ml of this solution diluted to 250 ml is equivalent to approximately 500 ppm of aluminum, 250 ppm of iron, 250 ppm of calcium, and 250 ppm of magnesium.)

Calcium Carbonate (CaCO_3) - C.P. low in alkali.

Ammonium Chloride (NH_4Cl) - reagent grade.

For Determination of Lithium

Radiation Buffer Solution

Weigh 31.77 g of sodium chloride (NaCl) and 23.85 g of potassium chloride (KCl) into a 400-ml beaker. Dissolve in distilled water and make to 500 ml. (This solution contains 25,000 ppm each

of sodium (Na) and potassium (K). When diluted 5 ml to 250 ml, the Na and K concentrations are approximately 500 ppm.)

Basic Lead Carbonate - reagent grade.

2M Ammonium Acetate 1M Acetic Acid Buffer Solution

Weigh 154 g of the reagent ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) into a 1-litre beaker. Dissolve in distilled water, add 60 ml glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$), and make to 1 litre.

Cupferron Solution 9%

Weigh 9 g of the reagent ($\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$) into a 250-ml beaker. Dissolve in 100 ml distilled water and filter if necessary. Cool in a tray of crushed ice.

Chloroform (CHCl_3) - reagent grade.

For Determination of Calcium

8-Quinolinol, 5% Solution in 2M Acetic Acid

Weigh 25 g of the reagent ($\text{C}_9\text{H}_7\text{ON}$) into a 400-ml beaker. Add 60 ml glacial acetic acid, 200 ml distilled water, and stir until in solution. Filter and make to 500 ml. Store in a polyethylene bottle.

2M Ammonium Acetate Solution

Weigh 77 g of the reagent ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) into a 600-ml beaker. Add approximately 300 ml distilled water, stir until in solution, and make to 500 ml. Store in a polyethylene bottle.

Chloroform - reagent grade.

Hydrogen Peroxide (H_2O_2 30%) - reagent grade.

Cupferron Solution 9%

Weigh 27 g of the reagent into a 400-ml beaker. Dissolve in 300 ml distilled water and filter if necessary. Cool in a tray of crushed ice.

5N Nitric Acid

Dilute 325 ml concentrated HNO_3 to 1 litre.

1:1 Tri-n-butyl Phosphate-Chloroform Extracting Solution

Mix 100 ml of tri-n-butyl phosphate with 100 ml of chloroform.

N-heptane (C_7H_{16}) - reagent grade.

6. SODIUM AND POTASSIUM DETERMINATION METHODS

Determination of Sodium and Potassium in Rocks and Minerals

Principle -

Iron, aluminum, magnesium, calcium, and phosphorus all interfere to some extent with the flame photometric determination of sodium and potassium. Two methods for the determination of these elements in rocks and minerals are given below, namely (a) a Radiation Buffer method and (b) a modified J. Lawrence Smith method⁽⁵⁾. In the first method the interfering ions are balanced out, and in the second they are removed.

In the Radiation Buffer procedure, the interference effects due to the above ions are compensated for by the addition of high concentrations of these interfering ions to both the standards and sample. This blanks out the effects of the small amounts present in the sample.

In the J. Lawrence Smith method, after the sample has been subjected to a calcium carbonate-ammonium chloride sinter the filtrate should contain only alkalis plus calcium. Practically all of the silicon, aluminum, iron, magnesium, and phosphorus is retained in the precipitate. Standards are prepared by addition of sodium and potassium to reagent blanks. In this way the amounts of alkalis present in the calcium carbonate and ammonium chloride

are exactly balanced out in both standards and sample. Also, the slight variation in calcium content between the standards and sample, due to calcium present in the sample, is not critical since the interference effect of calcium on the alkalis, using a propane flame, is slight.

Neither of these methods takes into consideration the interference effects of the alkalis on each other. Where the sodium concentration is much higher than that of potassium, and vice versa, equivalent amounts must be added to the standards.

(a) Radiation Buffer Method -

Preparation of standards:

Prepare 0, 1, 3, 5, 10, 15, 20 and 25 ppm sodium plus potassium standards by adding these amounts (in ml) of (Na + K) 100 ppm solution to 100-ml flasks containing 4 ml of radiation buffer solution. Make to volume. Prepare fresh every day.

Procedure:

Weigh a 0.2500-g sample into a 100-ml platinum dish. Carry a reagent blank through the procedure. Add 5 ml concentrated HClO_4 and evaporate to dryness on the hot plate. Add 5 ml 1:1 H_2SO_4 , 5 ml concentrated HCl, and 5 ml 48% HF. Evaporate to a small volume (approximately 10 ml), cool, wash down the sides of the dish, then add another 5 ml HCl and 5 ml HF. Evaporate to fumes of H_2SO_4 , cool, wash down the sides of the dish, and evaporate to complete dryness. Add approximately 25 ml water plus 3 drops of concentrated HCl and leave on the hot plate until the solution becomes clear. Transfer to a 400-ml beaker (using tongs to hold

the platinum dish in order to prevent contamination of sodium from the hands), then filter into a 250-ml volumetric flask. Add 10 ml of radiation buffer solution and make to volume. Determine both the % Na and the % K present in the sample and the reagent blank by reading on the Perkin-Elmer flame photometer between appropriate standards, using an air-propane flame. Subtract the blank results from the sample results.

1 ppm = 0.10% Na or K

$$\text{Factor } \frac{\text{Na}_2\text{O}}{2\text{Na}} = 1.3479 \quad \frac{\text{K}_2\text{O}}{2\text{K}} = 1.2046$$

For samples which are higher than 25 ppm, dilute the sample solution as required and add an equivalent amount of radiation buffer solution--e.g., for a 1:2 dilution, i.e. 50 ml of sample diluted to 100 ml, add another 2 ml of buffer solution; for a 1:4 dilution, i.e. 25 ml diluted to 100 ml, add another 3 ml of buffer solution.

Note: The above method applies only to samples that contain roughly equal amounts of both Na and K. Sodium will interfere with the potassium determination, and vice versa, when the ratio of one to the other is greater than one. For accurate analyses, estimate roughly the concentrations of both ions present in the sample, then prepare standards using the Na 100 ppm and the K 100 ppm solutions, i.e. add an equivalent amount of K to the Na standards, and vice versa.

(b) Modified J. Lawrence Smith Method -

Preparation of standards:

Weigh, on pieces of glazed paper, two blank preparations each containing 5 g of low alkali CaCO_3 and $\frac{1}{2}$ g of NH_4Cl . Mix well and transfer to 40-ml platinum crucibles. Cover with platinum lids and place each crucible in a hole which has been punched in a heavy asbestos sheet, so that one-third of its height is above the top of the sheet. Heat with a bunsen burner at a low temperature for about 15 minutes until NH_4Cl fumes cease to be evolved. Then increase the heat to full flame and maintain for 45 minutes. Cool, wash down the sides of the crucibles with distilled water (always holding the crucible with clean tongs), and transfer the crucibles plus contents to 600-ml steel beakers. Cover with distilled water and place on the hot plate for one hour. Remove the crucibles and let the solutions (covered) evaporate to about 150 ml. Filter hot, using Whatman #40 paper, into 250-ml flasks. Break up any lumps present with a thick glass rod. Wash the beakers and precipitates well with hot water. Add one drop of methyl red to the filtrates, and neutralize by the dropwise addition of concentrated HCl until the solutions just turn pink. Cool, and make to volume. Transfer 50-ml aliquots of these two blank solutions to eight 100-ml volumetric flasks. Prepare 0, 1, 3, 5, 10, 15, 20 and 25 ppm(Na + K) standards by adding these amounts (in ml) of (Na + K) 100 ppm solution. Make to volume.

Procedure:

Weigh, on glazed paper, 5 g of CaCO_3 , $\frac{1}{2}$ g of NH_4Cl , and 0.2500 g of finely ground sample (200 mesh). Mix well and transfer to a 40-ml platinum crucible. Treat exactly as for the standards but filter into a 500-ml volumetric flask. Neutralize, cool, and make to volume. (Check the completeness of decomposition by washing the precipitate into a beaker and dissolving with HCl. A clear solution indicates complete decomposition.) Determine both the % Na and % K present in the sample, by reading on the Perkin-Elmer 146 between appropriate standards, using an air-propane flame.

$$1 \text{ ppm} = 0.20\% \text{ Na or K}$$
$$\text{Factor } \frac{\text{Na}_2\text{O}}{2\text{Na}} = 1.3479 \quad \frac{\text{K}_2\text{O}}{2\text{K}} = 1.2046$$

For samples that are higher than 25 ppm, dilute the sample solution and prepare standards by adding (Na + K) 100 ppm solution to an equivalent amount of the blank solution--e.g., for a 1:2 dilution of the sample, i.e. 50 ml diluted to 100 ml, prepare standards by the addition of (Na + K) 100 ppm solution to 25 ml aliquots of the blank solution; for a 1:5 dilution, i.e. 20 ml diluted to 100 ml, prepare standards by addition to 10-ml aliquots.

Note 1: See note for Radiation Buffer method.

Note 2: Larger amounts of standards can be prepared, if desired, by weighing 8 blank samples, filtering into 500-ml flasks, and adding the requisite amounts of (Na + K) 1000 ppm solution. These solutions can be kept for approximately one month if stored in polyethylene bottles.

Applications of the Radiation Buffer Method -

- (1) All silicate-type materials except those high in phosphorus, e.g. granite, feldspar, mica, spodumene, lepidolite, clay, shale, tar sand, chlorite schist, serpentinite, nepheline syenite, and pollucite (the rubidium and cesium contents must be known and exact additions made to the standards).
- (2) Ceramic materials--e.g. silica sand, flint clay, fire brick, and glass.
- (3) Miscellaneous materials--e.g. iron ore, slags and concentrates (after removal of iron on the mercury cathode); niobium slags and concentrates, pyrochlore, and niocalite (after removal of Nb by hydrolysis in dilute H_2SO_4 solution); boiler scale; asbestos; coal ash; wood ash; sodium and/or potassium aluminum silicates; magnesium sludge; coal clinker (after ignition at $600^\circ C$); cryolite; and ilmenite (after removal of iron and titanium by a cupferron-chloroform extraction).

Applications of the Modified J. Lawrence Smith Method -

- (1) All materials listed under the Radiation Buffer method, plus those containing phosphorus but with the exception of those containing large amounts of niobium (i.e. niobium slags, concentrates, and minerals).
- (2) Refractory materials--e.g. kyanite, aluminum oxide, bauxite, and pyrophyllite muscovite.
- (3) Miscellaneous materials--e.g. cement, limestone, dolomite, marl, and fly ash.

7. LITHIUM DETERMINATION METHODS

Determination of Lithium in Minerals

Principle -

Iron, aluminum, phosphate, sodium, and potassium all interfere to some extent with the flame photometric determination of lithium. Accurate analysis requires some preliminary knowledge as to the amounts of these elements present in the sample, followed by equivalent additions to the standards. This is time-consuming, since it requires the preparation of separate standards for each sample. A more rapid and accurate method was developed ⁽⁶⁾ in which iron, aluminum, and also phosphate, were removed by a basic lead carbonate precipitation, and in which a buffer solution consisting of equal amounts of sodium and potassium ions was added to both standards and sample to give an approximate concentration of 500 ppm of each. The addition of a large amount of sodium and potassium in this way blanks out the small amounts present in the sample. The air-acetylene flame was used for the determination, since the effect of such high concentrations of alkalis on lithium is less than with a propane flame.

Preparation of Standards -

Prepare 0, 1, 3, 5, 10, 15, 20, 25, and 30 ppm lithium standards by adding these amounts (in ml) of Li 100 ppm solution to 100 ml-flasks. Add 2 ml of radiation buffer solution and make to volume.

Procedure -

Weigh a 0.2500-g sample into a 100-ml platinum dish. Add 5 ml concentrated HClO_4 and take to dryness on the hot plate. Cool, add 5 ml 1:1 H_2SO_4 , 5 ml concentrated HCl , 5 ml 48% HF , and allow to go into solution slowly at a moderate heat. Evaporate to a low volume, then add another 5 ml HCl and 5 ml HF . Take to complete dryness (i.e. until H_2SO_4 fumes cease to be evolved). Cool, add about 25 ml water and 1 ml of 10% H_2SO_4 and heat to dissolve the salts. When in solution transfer to a 400-ml beaker, add a few drops of methyl red, cover with a watch glass, and heat to boiling. Add basic lead carbonate slowly from a spatula until the solution is basic to methyl red (i.e. lemon yellow in colour). Filter hot through Whatman # 42 paper into a 400-ml beaker, washing both beaker and precipitate well with hot water. Add 5 ml 1:1 H_2SO_4 to the filtrate and evaporate to dryness. Wash down the sides of the beaker and again evaporate to dryness. Take up the residue with approximately 50 ml distilled water, heat, and filter through # 42 paper (to remove excess PbSO_4) into a 250-ml flask. Add 5 ml of

radiation buffer solution and make to volume. Read on the Perkin-Elmer flame photometer between appropriate lithium standards, using air-acetylene flame.

$$\begin{aligned} 1 \text{ ppm} &= 0.10\% \text{ Li} \\ \text{Factor } \frac{\text{Li}_2\text{O}}{2\text{Li}} &= 2.1527 \end{aligned}$$

For samples higher than 30 ppm Li, dilute 50 ml of sample plus 1 ml of radiation buffer to 100 ml.

Note: For phosphate-type minerals, e.g. amblygonite, add 5 ml of 10% H_2SO_4 to take up the residue in the platinum dish. Wash into the 400-ml beaker and neutralize most of the excess acid with concentrated NH_4OH . During evaporation of the filtrate to dryness, add 15 ml concentrated HNO_3 plus 5 ml concentrated HCl to destroy ammonium salts.

Determination of Lithium in Aluminum Metal and Alloys

Principle -

Lithium can be determined flame-photometrically in aluminum metal and alloys after removal of the aluminum by a cupferron-chloroform extraction at pH 3.6.

Preparation of Standards -

Prepare 1, 3, 5, 10, 15, 20, and 25 ppm Li standards by adding these amounts (in ml) of Li 100 ppm solution to 100 ml flasks. Make to volume.

Procedure -

Weigh a 0.5000-g sample of aluminum metal into a 250-ml beaker. Add about 25 ml distilled water and 10 ml concentrated HCl. Cover and place on the hot plate until in solution. Cool, then neutralize most of the excess acid with concentrated NH_4OH . Cool, then adjust the pH to approximately 0.5, using a pH meter and concentrated NH_4OH . Add 25 ml of 2M ammonium acetate 1M acetic acid buffer and make to 100 ml. Transfer a 20-ml aliquot to a 125-ml separatory funnel. Add 25 ml of cold, freshly prepared 9% cupferron solution, shake to coagulate the precipitate, then extract with 4 successive portions, i.e. 20, 10, 5, and 5 ml, of chloroform. Wash the aqueous layer into a 250-ml beaker and heat gently on the hot plate to remove excess chloroform. Then evaporate to dryness with the aid of 15 ml concentrated HNO_3 , 5 ml concentrated HCl, and 5 ml 1:1 H_2SO_4 . Wash down the sides of the beaker and evaporate to dryness again. Take up with approximately 50 ml distilled water, heat, cool, filter into a 200-ml flask, and make to volume. Read between appropriate Li standards, using the Perkin-Elmer flame photometer and an air-acetylene flame.

1 ppm = 0.20% Li

Note: Large amounts (i.e. greater than approximately 3%) of alloying constituents, e.g. iron, chromium or zinc, can be removed after the aluminum extraction by a mercury cathode separation. After evaporation of the aqueous layer to dryness, take up the residue with 2 ml 1:1 H_2SO_4 and approximately 100 ml water. Transfer to the mercury cathode and electrolyze for $\frac{1}{2}$ hour. Filter back into the original beaker and evaporate to dryness again, etc.

Determination of Small Amounts of Lithium in High-Purity Zinc Metal

Preparation of Standards -

As for "Determination of Lithium in Aluminum Metal and Alloys", see page 20.

Procedure -

Weigh a 1.0000-g sample of high-purity zinc into a 250-ml beaker. Add about 25 ml distilled water, 5 ml 1:1 H_2SO_4 , and 3 ml concentrated HCl. When solution is complete, evaporate to dryness on the hot plate. Add 1 ml 1:1 H_2SO_4 plus approximately 50 ml distilled water, and heat to dissolve the salts. Transfer to a mercury cathode cell and electrolyze for 1 hour. Filter back into the original beaker and evaporate to dryness. Wash down the sides and evaporate to dryness again. Take up the residue with about 15 ml distilled water, filter into a 50-ml flask, and make to volume. Read the lithium on the Perkin-Elmer flame photometer between appropriate standards, using air-acetylene flame.

$$1 \text{ ppm} = 0.0050\% \text{ Li}$$

For larger amounts of Li, dilute the sample as required.

Application -

Lithium in high-purity tin metal.

Determination of Small Amounts of Lithium, Sodium, and Potassium
in High-Purity Bismuth Metal

Preparation of Standards -

Prepare Li standards as in "Determination of Lithium in Aluminum Metal and Alloys", see page 20. Prepare 1, 3, 5, 10, 15, 20, and 25 ppm (Na + K) standards by adding these amounts (in ml) of (Na + K) 100 ppm solution to 100-ml flasks. Make to volume.

Procedure -

Weigh a 1.0000-g sample of high-purity bismuth metal into a 250-ml beaker. Add about 25 ml distilled water, 4 ml concentrated HNO_3 , and 3 ml concentrated HClO_4 to both the sample and a blank, and evaporate to fumes of HClO_4 . Cool, wash down the sides of the beakers, and evaporate to fumes again. Add another 1 ml concentrated HClO_4 , plus approximately 50 ml distilled water, and transfer both sample and blank to mercury cathode cells. Electrolyze for 1 hour, filter back into the original beakers, add 1 ml 1:1 H_2SO_4 , and evaporate to dryness. Cool, wash down the sides of the beakers, and evaporate to complete dryness. Take up the residue with about 15 ml distilled water, filter into 50-ml flasks, and make to volume. Read % Li, Na and K on the Perkin-Elmer flame photometer between appropriate standards, using air-propane flame for the Na and K determinations and air-acetylene flame for the Li. Determine % Na and K in the blank, and subtract from the results obtained for the sample.

1 ppm = 0.0050% Li, Na, or K.

Application -

Lithium in high-purity copper metal.

8. CALCIUM DETERMINATION METHODS

Determination of Calcium in Sandstones, Silica Sands, and Quartz

Principle -

The flame photometric method for calcium is ideally suited to the determination of calcium in sandstones, silica sands, and quartz, since these materials consist chiefly of silica plus small amounts of iron, aluminum and alkalies. The aluminum must be removed, since it suppresses the calcium results. The alkalies are not generally present in sufficient amounts to interfere.

Preparation of Standards -

Prepare 5, 10, 15, 20, and 25 ppm Ca standards by adding these amounts (in ml) of Ca 100 ppm solution to 100-ml flasks. Make to volume.

Procedure -

Weigh a 1.0000-g sample into a 100-ml platinum dish. Carry a reagent blank through the procedure. Add 5 ml concentrated HClO_4 and take to dryness. Add 10 ml concentrated HCl , 5 ml 48% HF and 3 ml 1:1 H_2SO_4 , and evaporate to fumes of H_2SO_4 . Cool, wash down the sides of the dish, add 10 ml concentrated HCl and 5 ml 48% HF , and take to complete dryness. Take up the residue with 4 drops concentrated HCl and approximately 20 ml distilled water. When all salts are in solution, cool, transfer to a 250-ml beaker, and adjust the pH to 1.8 to 2.0, using a pH meter, with

1:1 NH_4OH . Transfer to a 125-ml separatory funnel. Add 10 ml of a 5% solution of 8-quinolinol in 2M acetic acid and shake. Add 10 ml of 2M ammonium acetate solution and shake. Extract with four successive portions, i.e. 15, 10, 5 and 5 ml, of chloroform or until both layers are water-white. Discard the organic layer. Wash the aqueous layer back into the original beaker, heat gently to remove excess chloroform, then bring to dryness with the addition of 20 ml concentrated HNO_3 and 10 ml concentrated HCl to destroy ammonium salts. Wash down the sides of the beaker with water and evaporate to dryness again. Take up with water and 1 drop concentrated HCl , filter into a 100-ml flask, and make to volume. Determine the % Ca present in both the sample and the blank, by reading on the Perkin-Elmer flame photometer between appropriate Ca standards, using the 6200 A band and air-acetylene flame. Subtract the blank result from the sample result.

$$1 \text{ ppm} = 0.01\% \text{ Ca}$$

$$\text{Factor } \frac{\text{CaO}}{\text{Ca}} = 1.3992$$

For concentrations of Ca above 25 ppm, dilute as required.

Determination of Calcium and Lithium in Titanium Metal and Alloys

Principle -

Calcium and lithium can be determined flame-photometrically in titanium metal and alloys after removal of the titanium by a cupferron-chloroform extraction and of the aluminum by an 8-quinolinol-chloroform extraction. The aluminum, if present in small amounts, need not be removed if lithium only is to be determined. Cupferron-chloroform extraction also serves to remove some alloying constituents, e.g. molybdenum, zirconium, iron, and vanadium. Large amounts of chromium, copper, cobalt and nickel can be removed by a mercury cathode separation.

Preparation of Standards -

Prepare Ca standards as in "Determination of Calcium in Sandstones, Silica Sands, and Quartz", see page 24.

Prepare Li standards as in "Determination of Lithium in Aluminum Metal and Alloys", see page 20.

Procedure -

Determination of Ca: Weigh a 0.5000-g sample into a 600-ml beaker. Carry a reagent blank through the entire procedure. Add approximately 100 ml distilled water, cover, and add slowly 35 ml concentrated H_2SO_4 . When all the sample is in solution, add 3 ml of 30% H_2O_2 and boil until the solution becomes colourless. Remove the watch glass, wash down the sides of the beaker, and evaporate to fumes of H_2SO_4 to remove excess H_2O_2 . Cool, wash down the sides of the beaker, and evaporate to fumes again. Cool,

add about 50 ml of water, and cool in a tray of crushed ice.

Transfer to a 500-ml separatory funnel, add 105 ml of cold, freshly prepared 9% cupferron solution, and shake to coagulate the precipitate.

Add 50 ml of chloroform, shake for a few minutes, let stand for 5 minutes, and then drain off the organic layer. Add another

5 ml of cupferron solution (a white flash at this point indicates

complete precipitation of the Ti). Extract with 20, 10, 10, 10 ml (etc.)

portions of chloroform until both layers are water-white. Drain the

aqueous layer back into the original beaker, cover, and heat gently

on a warm hot plate to remove excess chloroform. Evaporate to

about 75 ml, add 20 ml concentrated HNO_3 and 10 ml concentrated

HCl to destroy excess cupferron, and then evaporate to dryness.

Cool, wash down the sides of the beaker, and evaporate to complete

dryness. Add approximately 25 ml water and 0.5 ml concentrated

HCl . Heat until all residue is in solution, cool, and transfer to

a 250-ml beaker. Adjust the pH to 1.8 to 2.0, using a pH meter

with 1:1 NH_4OH . Transfer to a 125-ml separatory funnel. Add

10 ml of a solution of 5% 8-quinolinol in 2M acetic acid and shake.

Add 10 ml of 2M ammonium acetate buffer and shake to coagulate

the precipitate. Extract with 20, 10, 5 and 5 ml portions of chloroform.

Wash the aqueous layer back into the 250-ml beaker, cover, and heat gently to remove excess chloroform. Then evaporate to dryness

with the addition of 15 ml concentrated HNO_3 and 5 ml concentrated

HCl to destroy ammonium salts. Wash down the sides of the beaker

and evaporate to complete dryness. Take up the residue with about 20 ml water, heat, cool, and filter into a 50-ml flask. Make to volume. Determine % Ca in both sample and blank, reading between appropriate Ca standards on the Perkin-Elmer flame photometer, using the 6200 A band and air-acetylene flame. Subtract the blank result from the sample result.

$$1 \text{ ppm} = 0.01\% \text{ Ca}$$

For samples that are higher than 25 ppm Ca, dilute as required.

Determination of Li: Li can be determined on the above solution; or, if Li only is to be determined, a shorter method may be employed, viz., after solution of the sample and evaporation to fumes of H_2SO_4 , cool, add about 150 ml water, and allow to cool to room temperature. Make up to 250 ml in a volumetric flask. Transfer a 50-ml aliquot to a 125-ml separatory funnel, add 25 ml of cold, freshly prepared 9% cupferron solution, shake, and extract 20, 10, 5 and 5 ml of chloroform. Evaporate the aqueous layer to dryness, etc., as above, and filter into a 50-ml volumetric flask. Read the Li between appropriate Li standards, using an air-acetylene flame.

$$1 \text{ ppm} = 0.05\% \text{ Li}$$

Application -

Determination of Calcium and Lithium in vanadium metal.

Determination of Calcium in Impure Uranium Oxides

Principle -

Calcium can be determined flame-photometrically in impure uranium oxides after removal of the uranium by extraction as uranyl nitrate with tri-n-butyl phosphate, and after removal of possible small amounts of aluminum with 8-quinolinol and chloroform.

Preparation of Standards -

As for "Determination of Calcium in Sandstones, Silica Sands, and Quartz", see page 24.

Analyze the sample for the approximate Na and K contents and add these amounts to the standards.

Procedure -

Weigh a 1.0000-g sample into a 250-ml beaker. Add 30 ml of 5N HNO₃ to both the sample and a reagent blank. Heat gently, keeping covered until in solution. Cool, wash into a 125-ml separatory funnel with approximately 20 ml of 5N HNO₃. Add 40 ml of extracting solution and shake for about 3 minutes. Allow to settle and drain off the organic layer. Add another 10 ml of extracting solution plus 5 ml of chloroform, shake, allow to settle, and drain off the organic layer. Clean the aqueous layer with two successive extractions with 5 ml of chloroform. Then add 10 ml of n-heptane and shake. Rinse out the stem of the funnel with distilled water, then drain the aqueous layer into the original beaker, making sure

that none of the n-heptane layer is drained off with the aqueous. Add 10 ml of 5N HNO₃ to the funnel, shake, allow to settle, and add the lower acid layer to the aqueous in the beaker. Repeat twice more with 10-ml portions of 5N HNO₃. Evaporate both sample and blank solutions to dryness with the addition of 5 ml of 1:1 H₂SO₄. (If soluble silica is present in the sample, evaporate the aqueous layer down to a low volume, transfer to a platinum dish, treat with 1 ml 48% HF plus 5 ml 1:1 H₂SO₄, and evaporate to dryness.) Take up the residue with approximately 25 ml water and 5 drops concentrated HCl, and heat until in solution. Cool, adjust the pH to 1.8 to 2.0 with 1:1 NH₄OH, and transfer to a 125-ml separatory funnel. Add 15 ml of a solution of 5% 8-quinolinol in 2M acetic acid and shake. Add 10 ml of 2M ammonium acetate buffer and shake. Extract the aluminum with four successive portions of chloroform, i.e. 20, 10, 5, and 5 ml. Drain the aqueous layer back into the original beaker and evaporate to dryness with the addition of 15 ml concentrated HNO₃, 5 ml concentrated HCl and 5 ml 1:1 H₂SO₄. Wash down the sides of the beaker and evaporate to complete dryness. Add about 20 ml of water to the residue in the beaker, boil until in solution, cool, filter into a 50-ml flask, and make to volume. (If all the residue does not go into solution, add one or two drops of HCl. Also add an equivalent amount to the standards.) Estimate by flame photometry the approximate Na and K contents of the sample and add these amounts to the Ca standards.

Determine % Ca in both the sample and the blank, on the Perkin-Elmer flame photometer, by reading between appropriate Ca standards, using air-acetylene flame and the 6200 A band. Subtract the blank result from the sample result.

$$1 \text{ ppm} = 0.005\% \text{ Ca}$$

Note 1: The chloroform and n-heptane scrubbing of the aqueous layer is to ensure complete removal of phosphate. Scrubbing of the n-heptane layer with 5N HNO₃ is to regain the last few drops of solution that were left with the n-heptane layer when the aqueous layer was first drained off.

Note 2: The chloroform in the extracting solution raises the density of the extracting solution so that it is greater than that of the aqueous layer.

9. ANALYSIS OF MISCELLANEOUS MATERIALS

For Sodium and/or Potassium Determination

- (1) Salt Cores - Dissolve in water. Add Na to K standards and vice versa.
- (2) Alkali Fluoro Titanates, e.g. Na_2TiF_6 and K_2TiF_6 - Remove fluoride ion with H_2SO_4 in a platinum dish, hydrolyze Ti in hot dilute H_2SO_4 solution, filter, and wash with hot water. Evaporate to dryness. Read between Na standards for Na_2TiF_6 , and between K standards for K_2TiF_6 .
- (3) Alkali Chloro Titanates, e.g. K_2TiCl_6 - Hydrolyze Ti in hot dilute H_2SO_4 , etc., as in (2).
- (4) Water Glass (Sodium Silicate) - Weigh in a weighing bottle. Wash into a plastic beaker with hot water, make to volume in a volumetric flask, and immediately transfer to a plastic bottle. Aliquot into a platinum dish and evaporate to dryness with HF and H_2SO_4 . Read between Na standards.
- (5) Quartz - Treat sample and blank with HF and H_2SO_4 and evaporate to dryness. Read between (Na + K) standards.
- (6) Lithium Metal (7) - Weigh under argon in a dry box. Dissolve on ice (prepared from distilled water) in a plastic or stainless steel beaker. Neutralize to methyl red with concentrated HCl. Evaporate an equivalent volume of HCl to dryness for the blank and make up to the same volume as the sample. Read between (Na + K) standards.

For Lithium Determination

- (1) Lithium Silicate (Li_2SiO_3) - Dissolve with HF and H_2SO_4 in a platinum dish and evaporate to dryness. Read between Li standards.
- (2) Lithium Fluoro Titanate (Li_2TiF_6) and Lithium Titanate (Li_2TiO_3) - see (2) above.
- (3) Lithium Magnesium Alloys - Dissolve in HCl and evaporate down to a syrupy consistency twice to remove all acid. Read between Li standards containing an equivalent concentration of Mg (prepared from pure Mg metal).
- (4) Lithium Fluoride (LiF) - Remove fluoride ion with H_2SO_4 . Read between Li standards.
- (5) Chromium Zinc Alloys - Dissolve in HClO_4 or H_2SO_4 . Aliquot, and remove Cr and Zn with the mercury cathode. Read between Li standards.
- (6) Chromium Titanium Alloys - Dissolve in H_2SO_4 and H_2O_2 . Evaporate to fumes twice to remove H_2O_2 . Aliquot, and extract Ti with cupferron and chloroform. Remove Cr on the mercury cathode. Read between Li standards.

For Calcium Determination

- (1) Silicon (Si) - Dissolve a large sample weight (in the order of 5 g) and a blank in a platinum dish with HNO_3 plus the dropwise addition of HF. Evaporate to dryness with H_2SO_4 . Adjust the pH to

1.8 to 2.0 and extract Al with 8-quinolinol and chloroform. Evaporate to dryness, make to a small volume (50 ml), and read between Ca standards.

10. REFERENCES

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