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GEAP-3273

COLLECTED METHODS

for

ANALYSIS OF SODIUM METAL

by

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Prepared For

ATOMICS INTERNATIONAL
A Division of North American Aviation, Inc.

Under

Contract No. N8-S-452

October 15, 1959

Vallecitos Atomic Laboratory
Atomic Power Equipment Department
GENERAL ELECTRIC COMPANY
Pleasanton, California

U N C L A S S I F I E D

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COLLECTED METHODS FOR ANALYSIS OF SODIUM METAL

SUMMARY

Methods for analyzing chemical impurities in sodium metal samples are presented. Chemical analysis was used to determine the following impurities: Calcium, Carbon, Chromium, Iron, Lithium, Nickel, Oxygen, Potassium, and Zirconium. Spectrographic analysis was used to determine many other impurities. Sodium samples obtained from experimental apparatus operated as part of the work being conducted for Atomics International were analyzed by these methods.

INTRODUCTION

In July 1958 the Atomic Power Equipment Department of the General Electric Company undertook a program to investigate the characteristics of plugs formed by impurities in sodium; to determine the rate of diffusion of sodium oxide in molten sodium; and to obtain information on sodium oxide and its removal by the cold trap method. This report contains the methods collected and developed for use in the chemical analysis of sodium metal from the plug growth facility, the purification loop, and the diffusion-cell assembly.

In all cases, except in the analysis for oxygen, the sodium metal is dissolved in methanol or water prior to analysis. Since the reaction is accompanied by the liberation of heat and the evolution of hydrogen, care must be exercised in the dissolution. A cover of inert gas is used and a container of Met-L-X powder is a necessary safety precaution. Although the precautions necessary to safely handle sodium metal make some procedures lengthy, the methods are adapted to routine laboratory use. References are given to assist the chemist with more complex samples.

I. CALCIUM IN SODIUM

Abstract

Calcium is titrated to a visible end point with an EDTA salt (Disodium ethylene-diaminetetraacetate dihydrate). Calcein indicator is employed to make the method applicable in the presence of magnesium.

Reagents and Apparatus

Absolute Methanol

Hydroxide-Cyanide solution, (1N sodium hydroxide and 0.7N potassium cyanide)

Calcein Indicator, 2% solution; keep in foil covered container.,
G. Fredrick Smith Company, Columbus, Ohio

Iceland Spar (designated for standardizing), J. T. Baker Chemical Co.

0.002M Standard EDTA solution

Microscope illuminator

Lamp, G. E., Type. 16-1/2 - 29 (100 watts) 120V.

Three Kodak Wratten Filters #78AA.

Magnetic stirrer

Microburet

Procedure

1. Dissolve the sample in an inert atmosphere by the addition of small pieces to methanol. Add an equal volume of deionized water and heat carefully to evaporate the methanol. Cool.
2. To a sample aliquot, add 1 ml. hydroxide-cyanide solution and 1 drop of 2% calcein indicator solution.
3. Prepare blank in same manner, substitute deionized water for the sample. (Note 1).
4. Illuminate samples with the triple filtered microscope illuminator -- exclude other light. The blank appears pink and the sample greenish-yellow.
5. Titrate sample with standard EDTA (Note 2) while stirring continuously. (Note 3).

6. The end point is reached when the last trace of yellow is gone and the sample matches the blank in color.

Notes

1. A given blank should not be used with samples prepared appreciably later because the color deteriorates with time.
2. A 0.001M solution of Iceland Spar in hydrochloric acid is used to standardize the EDTA solution.
3. Due to the high pH (> 11), the calcium salts tend to precipitate. To prevent false end points, vigorous stirring is necessary.
4. Magnesium does not interfere in a 100 molar excess. It only interferes when present in large enough quantities to precipitate visibly with the hydroxide-cyanide solution.

Reference

Socular, S. J., and Salach, J. I., Analytical Chem. 31, 473 (1959).

II. CARBON IN SODIUM

Abstract

The sample is dissolved by dropwise addition of deionized water under an inert gas, acidified, and evaporated to near dryness. The carbon is oxidized to carbon dioxide and measured. A high carbon blank is inherent in the method. (Note 1).

Reagents and Apparatus

Pepkowitz carbon apparatus

Van Slyke Oxidizing Fluid

13 gms of Chromic Acid

85 ml of 85% orthophosphoric acid

165 ml of fuming sulfuric acid

Heat gradually to 140°C with stirring, cool to about 80°C, and finish cooling under vacuum in a desiccator.

5M sulfuric acid

Liquid nitrogen

Alcohol Slush Mixture (-100° to -105°C)

Carefully add liquid nitrogen to methanol containing up to 1/3 its volume water in a Dewar flask and stir vigorously. Maintain level by periodic additions of liquid nitrogen during the day. If the slush freezes, add a few ml of methanol.

Fisher-Snelling "Hot-Spot" Heater

Procedure

Lubricate stopcocks on the reaction vessel lid with sirupy phosphoric acid. Evacuate the system to the gasometer stopcock to about 2 microns. Flame the cold trap during evacuation to remove surface moisture.

If necessary, wrap the sodium sample in a copper sheet and smash with a hammer. Cut into small pieces and dissolve by dropwise addition of 5 ml of deionized water under inert gas in the reaction vessel. Neutralize the caustic solution with 5M sulfuric acid and add 10% excess. Evaporate to near dryness with a "hot-spot" heater, maintaining the inert gas flow to speed evaporation.

Attach the combustion tube to the apparatus and pass purified oxygen through the vessel and out the leveling bottle to remove air. Turn off the oxygen and connect the vessel with the gasometer. Add 5 ml of Van Slyke fluid and heat at incipient boiling for 5 minutes.

Sweep the combustion products into the gasometer with oxygen until it is full. The combustion products are slowly released into the evacuated system and condensed in the cold trap with liquid nitrogen. When the leveling solution has raised the float valve shut off the gasometer and flush it with oxygen in preparation for the next run while measuring the carbon dioxide. This flushing is important.

After a few minutes to condense the gases in the cold trap, open the vacuum line to remove the oxygen. After most of the oxygen is removed, connect the McLeod gage with the pump. Continue the pumping until the pressure drops to 2 microns.

Isolate the pump and replace the liquid nitrogen with the alcohol slush mixture. The carbon dioxide sublimates into the measuring volume. The pressure is followed until a constant value is obtained (About 12 minutes).

Calculations

$$\text{Mg of Carbon} = (h_1^2 - h_2^2) K$$

Where h_1 is the length of the gas column in the sealed capillary of the McLeod gage in mm. for the sample.

h_2 is the length of the gas column in the sealed capillary for the blank in mm.

K is the experimentally determined constant for the whole system determined by carrying standard samples through the procedure.

Note

1. This method, although workable, was found to be unsatisfactory for the low range of analyses desired due to the high carbon blank inherent in the method.

References

1. Pepkowitz, L. P., and Porter, J. T., Analytical Chem. 28, 1606, (1956).
2. Pepkowitz, L. P., and Moak, W. D., Analytical Chem. 26, 1022, (1954).
3. The Analysis of Sodium Metal and Sodium-Potassium Alloy (Collected Capenhurst Methods), IGO-AM/CA110 (Unclassified), U.K.A.E.G.I.G., (March, 1958).

III. CHROMIUM IN SODIUM

Abstract

Chromium is determined colorimetrically with s-Diphenylcarbazide reagent.

Reagents

Absolute Methanol

0.1N Silver Nitrate solution

1N Ammonium Persulfate

6N Sulfuric Acid

1:10 (~1N) Hydrochloric Acid

1:100 (~0.1N) Hydrochloric Acid

0.1% Methyl Orange indicator

2N Sodium Hydroxide

s-Diphenylcarbazide solution, 4 grams of phthalic anhydride and
0.25 gm. of s-diphenylcarbazide in 100 ml. of 95% ethanol
(Stable 1 month).

Procedure

Dissolve the sample in an inert atmosphere by the addition of small pieces to methanol. Add an equal volume of deionized water and heat carefully to evaporate the methanol.

Take an aliquot to contain 0.0005-0.015 mg. of chromium. Add 5 ml. of 0.1N silver nitrate. Mix and add 10 ml. of 1N ammonium persulfate. Boil for 30 minutes and while still hot add 20 ml. of 1:10 hydrochloric acid. Filter and wash the silver chloride on the filter with 1:100 hydrochloric acid.

Dilute to about 60 ml. and make approximately neutral to methyl orange with 2N NaOH without adding indicator (approx. pH 4). Adjust the acidity of the approximately neutral solution by adding 3.3 ml. of 4N sulfuric acid and transfer to a 100 ml. volumetric flask. Add 1 ml. of the reagent and dilute to volume.

Determine optical density against a reagent blank at 540 mμ in a 10 cm Beckman cell within 5 minutes. Read ppm from a calibration curve obtained with standard solutions.

Reference

1. Snell, F. D., and Snell, C. T., Colorimetric Methods of Analysis, New York, D. Van Nostrand Co., Inc. (1957).

IV. IRON IN SODIUM

Abstract

Iron is determined colorimetrically with o-phenanthroline reagent.

Reagents

Absolute Methanol

Hydrazine Hydrate, 85%

o-phenanthroline reagent, dissolve 0.5 gm. in 5 drops conc. hydrochloric acid and 1 ml. deionized water. Add 100 ml. water. Add 200 gm. sodium acetate and 200 ml. glacial acetic acid. Warm, stir until dissolved and dilute to 500 ml.

Procedure

Dissolve the sample in an inert atmosphere by the addition of small pieces to methanol. Add an equal volume of deionized water and heat carefully to evaporate the methanol.

Take an aliquot to contain 0.005-0.12 mg. of iron. Evaporate if necessary. Add sample aliquot to a 50 ml. flask containing 2.5 ml. of conc. hydrochloric acid, 2 ml. of o-phenanthroline reagent, and 5 drops of hydrazine hydrate. If pH is not 3-5, adjust with conc. hydrochloric acid or conc. ammonium hydroxide.

Wait 30 min. for complete reduction of iron and determine optical density with a 520 mu filter in a 4 cm Klett cell or a 10 cm Beckman cell at 510 mu. Read against the original solution instead of a reagent blank since other colors from material may cause interferences in true iron reading.

Read ppm from calibration curve obtained with standard solutions.

References

1. Sandell, Ernest, Colorimetric Determination of Traces of Metals, 2nd Ed. New York, Interscience Publishers, (1950).
2. ASTM Standards, Pennsylvania, American Society for Testing Materials, (1955).

V. LITHIUM IN SODIUM

Abstract

Lithium is determined by flame photometry.

Reagents and Apparatus

Standard lithium solutions

Beckman Model DU Flame Spectrophotometer

Didymium Filter

Hydrochloric Acid

Procedure

Dissolve the sample by dropwise addition of deionized water in an inert atmosphere. Acidify with hydrochloric acid.

Determine the approximate sample composition by reading trial samples. Prepare standard lithium solutions containing anions and cations to as closely match the sample composition as possible. Usually a set of standards must be made for each sample since compositions vary.

Determine luminosity (% transmittance scale) of the sample against a deionized water blank using a Didymium Filter. Use the following settings:

<u>Wave Length</u>	<u>Slit Width</u>	<u>Sensitivity</u>
670 mu	0.1 - 0.2 mm	Two to four turns from clock-wise limit

Read ppm lithium from a calibration curve prepared from standard solutions.

Reference

1. Farquhar, Analysis of the Alkali Metals, American Potash & Chemical Corporation, Trona, California, (Meeting of the American Chemical Society, September, 1958, Chicago, Ill.)
2. F. Burriel-Martí, J. Ramírez-Muñoz, Flame Photometry A Manual of Methods and Applications, New York, Elsevier Publishing Company (1957).

VI. NICKEL IN SODIUM

Abstract

Nickel is determined colorimetrically with dimethylglyoxime reagent.

Reagents

Absolute Methanol

Ammonium Citrate Solution, 540 gm. per liter, filter if necessary

Dimethylglyoxime, 1.0 gm. in 500 ml. of ammonium hydroxide
dilute to one liter, make fresh, good for one month

Iodine Solution, dissolve 8 gm. of potassium iodide and 2.6 gm. of
iodine in a minimum of water and dilute to one liter.

Procedure

Dissolve the sample in an inert atmosphere by the addition of small pieces to methanol. Add an equal volume of deionized water and heat carefully to evaporate the methanol.

To an aliquot containing not more than 0.3 mg. nickel in a 50 ml volumetric flask add in the following order:

5 ml. ammonium citrate solution
5 ml. iodine solution
10 ml. dimethylglyoxime

Dilute to mark and mix. Determine optical density after 10 minutes against a reagent blank at 540 mμ in a 10 cm Beckman cell.

Read ppm nickel from a calibration curve prepared with standard solutions.

Reference

ASTM Methods for Chemical Analysis of Metals, Pennsylvania,
American Society for Testing Materials, (1956).

VII. SODIUM MONOXIDE

A. Major Constituent

Abstract

The "free" sodium is measured by hydrogen evolution. Total sodium and sodium bicarbonate are determined by titration. The sodium monoxide is determined by difference. It is assumed only sodium, sodium bicarbonate, and sodium monoxide are present.⁽³⁾

Reagents and Apparatus

Edwards Analyzer^(1,2)

Absolute Methanol

3N Standard Hydrochloric Acid

Inert Gas Supply

pH Meter

Procedure

Dissolve the sample by drop-wise addition of methanol (Note 1), measuring the hydrogen evolved using the Edwards Analyzer. Add an equal volume of deionized water to the sample and heat carefully to evaporate the methanol (Note 2). Cool and titrate the solution potentiometrically to the phenolphthalein and methyl orange end points. Plot $\Delta E / \Delta V$ against milliliters of standard acid to determine the end points.

Notes

1. Cooling is necessary after the addition of the first few drops of methanol.
2. A stream of inert gas is used to speed evaporation. Errors will result in the determination of the end points if the methanol is not evaporated.

Calculations

$$\% \text{Na}_2\text{O} = \left[\frac{\text{mg. total sodium}}{\text{mg. sample}} - \frac{\text{mg. Na from NaHCO}_3}{\text{mg. sample}} - \frac{\text{mg. (free) Na}}{\text{mg. sample}} \right] \quad (135)$$

$$\% \text{NaHCO}_3 = \left[\frac{(\text{MO end point} - \text{PP end point}) * (N_{\text{HCl}}) (84.02)}{\text{mg. sample}} \right] \quad (100)$$

* Measured in ml. of acid

$$\% \text{ Na (Free)} = \left[\frac{(\text{cc. of hydrogen}) * (46)}{(22.4) \text{ (mg. sample)}} \right] \quad (100)$$

* at Std. Temperature, Pressure

References

1. Edwards, A. H., Analyst 71, 521-24 (1946).
2. Sittig, Marshal, Sodium, Its Manufacture, Properties and Uses, New York, Reinhold Publishing Corporation (1956).
3. Yamaguchi, S., Tokyo Institute of Physical Chemistry Research Science Papers, 37, 424, (1946).

VII. SODIUM MONOXIDE

B. Minor Constituent

More trouble-free operation is provided by apparatus of modified design employed in the mercury amalgamation method for the determination of oxygen in sodium. Procedures are given for operation and standardization of the method. A discussion of the results and the difficulties encountered is given.

Reagents

Highest purity triple distilled filtered mercury

3N Standard Hydrochloric acid

3N Standard Sodium Hydroxide

0.005N Standard Hydrochloric Acid

Neutralized water, neutralize deionized water to phenolphthalein end point. with dilute sodium hydroxide and swirl in air until the color just disappears.

Apparatus

The high vacuum apparatus of Williams and Miller⁽²⁾ is used with some modifications. An all-glass high vacuum apparatus is used to eliminate the diffusion of oxygen through the thin rubber tubing connections present in the original mercury amalgamation apparatus⁽¹⁾. Williams and Miller also incorporated a mercury "shower" system to rinse the walls of the extractor column and magnetic stirring and breaking of the sample capsule.

Modifications were made in the Williams and Miller apparatus to reduce breakage and to provide thorough purging during the transfer of samples into the extraction column. The apparatus is presented in Figures 1 and 2.

The mercury reservoir is divided into two parts connected with Tygon tubing to remove the strain on the system caused by the weight of the mercury. The stopcocks (Figure 2) have been designed to purge both the glass frit and the standard taper joint space during the time the shower head is removed to introduce a sample. The extractor column has been lengthened 5 cm. above the upper stopcock to insure thorough purging when it is necessary to introduce samples. Smaller bore stopcocks were replaced with 4 mm bore stopcocks because the heavier sidearms reduced breakage. The joint at the top of the receiver flask has been changed to a ball and socket joint.

EXTRACTION APPARATUS

FIGURE 1

FIGURE 2

DETAILS OF MERCURY SHOWER HEAD

A compact vacuum-inert gas manifold was designed for operation of two extraction columns at one time (Figure 1). If desired a vacuum gage tube may be attached to the manifold between the two stopcocks.

The details of the stainless steel case for the iron breaker and stirring bar are presented in Figure 4. Samples not enclosed in glass capsules can be transferred to the extractor column from a dry box with use of a transfer tube (Figure 4), or a sample thief.⁽⁷⁾

A compressed air stream is used for cooling the extractor column after extraction. The receiving flasks are supported by Fisher Micro Lab-Jacks to facilitate removal.

The glassware is cleaned of stopcock grease with chloroform after use. The apparatus is then cleaned in boiling 1:1 nitric acid, rinsed with deionized water until neutral, and dried in an oven until used.

A sodium-potassium bubbler is used for purification of the inert purge gas⁽⁴⁾. Silverman and Bradshaw have shown that this procedure reduces the oxygen content of helium gas from 5 to 0.1 ppm⁽⁵⁾.

A triple distillation unit is used to provide pure sodium for standardization, see Figure 3. A tube for filling the unit with sodium is illustrated in Figure 4. The six sample bulbs, (only two shown in Figure 3) may be filled with known amounts of mercuric oxide or left empty as blanks.

The infra-red bake-out oven for use in sodium distillation is constructed of two Corning Pyrex Radiant Heaters. The panels provide a total of 5700 watts and a maximum temperature of 350°C. The heaters are mounted on a frame designed to be supported by two 1/2" diameter rods for easy attachment and removal. The ends, rear, and bottom of the oven are made of removable 3/16" transite panels.

Procedure

A. Extraction

Take the apparatus hot from the oven, assemble, evacuate, and flame to remove the adsorbed gases. Flush with inert gas, purge all stopcock bores, and re-evacuate. Close both stopcocks on the extractor column and add approximately 10 ml of mercury. Break the sample bulb by dropping the stainless steel encased stirring bar on it. As the sample bulb breaks, immediately add another 20 ml of mercury, allowing the shower system to rinse down the walls of the column. Stir the amalgam vigorously with the stirring bar by means of an external magnet and gently flame the column during extraction. Cool for five minutes with a cold air stream⁽³⁾. Drain all but 2 or 3 ml. of the amalgam into the receiving flask. Open the upper column stopcock during draining of the amalgam to

TRIPLE DISTILLATION APPARATUS

FIGURE 3

FIGURE 4

STIRRING BAR
(PRESS FIT STAINLESS
STEEL CASE AND CAPS)

TRANSFER TUBE

re-evacuate the column, as a precaution against leaks. Repeat the extraction process with 20 ml portions of mercury and flaming of the column during extraction until a test^(a) shows extraction is complete.

The dissolution and titration are the same as that described by Pepkowitz and Judd⁽¹⁾. The sodium monoxide is determined by dissolving in neutralized water and titrating with 0.005N hydrochloric acid to the phenolphthalein end point. The sodium sample size is obtained by adding a known excess of 3N hydrochloric acid to the sodium amalgam, allowing to react, and back titrating with 3N sodium hydroxide.

Footnote:

- (a) A small amount of the amalgam is run into a flask containing neutralized water. Absence of basicity indicates that extraction is complete.

B. Standardization

The steps in sodium distillation and preparation of standards are:

1. Set up triple distillation apparatus (Figure 3) and seal on sample bulbs if necessary.
2. Evacuate and check for leaks.
3. Enclose in oven and bake-out @ 350° - 450°C for one hour. (The bake-out oven used by the author obtained a maximum temperature of 350°C).
4. Remove infra-red bake-out oven and cool.
5. Attach filling tube and add approximately 125 ml. of sodium from a heated pressurized sodium "pot" (similar to that used for shipping sodium-potassium) under an inert gas purge.
6. Cool and seal.
7. Re-evacuate to 5×10^{-6} mm. of mercury.
8. Bake-out at 325° for approximately 10 minutes.
9. Complete distillation with a hand torch using a large gas-air flame.
10. Seal-off and remove sample bulbs.

C. Experimental

Various writers have stated that the major difficulty in the Pepkowitz method is in breaking the bulbs containing the sample.

This same difficulty was encountered at first and was complicated by breakage of the glass enclosed stirring bar. Welding the stirring bar magnet in a stainless steel case provided a solution. The heavier weight of the encased stirring bar breaks the sample bulb in two or three drops and provides deeper stirring action.

Samples sealed in glass bulbs provide no problem in sampling. However, samples which must be transferred in open metal containers present the problem of oxidation during the transfer into the extraction column. Thorough purging of the entire apparatus is necessary to prevent the presence of any trapped air at the start of the pumpdown. It is necessary to purge the mercury shower head and glass frit as well as the extraction column. The apparatus is designed for speed of operation and thorough purging, both of which are necessary to prevent oxidation and to provide accuracy.

The triple distillation bake-out procedure is a convenient way to obtain pure sodium for standardization. The oxygen content of sodium distilled by this procedure is given in Table I. The results compare favorably with those published in the literature (1,2,4). Additional standardization was attempted by adding known amounts of oxygen as mercuric oxide to the sample bulbs. Poor recoveries were obtained. The cause has not yet been determined. It is most probably caused by decomposition of the mercuric oxide during the bake-out process, although incomplete reduction of the mercuric oxide before analysis may also be the reason.

Initially, some difficulty was experienced with crystallization of the amalgam during the first extraction⁽⁶⁾. It is possible this would allow some of the sodium monoxide to be drained into the receiving flask. In order to prevent formation of solid amalgam, the initial portion of mercury added during the first extraction was increased to 30 ml.

TABLE I

Oxygen Content of Triple Distilled Sodium

<u>Oxygen %</u>	<u>Deviation from Mean</u>
0.002	0.0004
0.001	0.0014
0.002	0.0004
0.004	0.0016
0.002	0.0004
0.004	0.0016
<u>0.002</u>	<u>0.0004</u>
mean 0.0024	<u>± 0.0009</u>

References

1. Pepkowitz, L. P., and Judd, W. C., Analytical Chemistry 22, 1283, (1950).
2. Williams, D. D., and Miller, R. R., Analytical Chemistry 23, 1865, (1951).
3. The Analysis of Sodium Metal and Sodium-Potassium Alloy (Collected Capenhurst Methods) IGO-AM/CA-110 (Unclassified) U.K.A.E.A.I.G., (March, 1958).
4. Pepkowitz, L. P., and Judd, W. C., and Downer, R. J., Analytical Chemistry 26, 246, (1954).
5. Silverman, L., and Bradshaw, W., North American Aviation, Special Report 892.
6. Hansen, Max, Constitution of Binary Alloys, 2nd Ed., New York, McGraw-Hill Book Company, Inc. (1958).
7. Jackson, C. B., and Adams, R. M., Liquid Metals Handbook, Navexos P-733 (Rev.), Washington, D. C., U. S. Govt. Printing Office (1952).

VIII. POTASSIUM IN SODIUM

Abstract

Potassium is determined by flame photometry.

Reagents and Apparatus

Standard potassium solutions

Beckman Model DU flame spectrophotometer

Didymium Filter

Hydrochloric Acid

Procedure

Dissolve the sample by dropwise addition of deionized water in an inert atmosphere. Acidify with hydrochloric acid.

Determine the approximate sample composition by reading trial samples. Prepare standard potassium solutions containing anions and cations to as closely match the sample composition as possible. Usually a set of standards must be made for each sample since compositions vary.

Determine luminosity (% transmittance scale) of the sample against deionized water blank using a Didymium filter.

Use the following settings:

<u>Wave Length</u>	<u>Slit Width</u>	<u>Sensitivity</u>
766 mμ	0.05-0.15	Two to four turns from clockwise limit

Read ppm potassium from calibration curve prepared from standard solutions.

Reference

1. Farquhar, Analysis of the Alkali Metals, American Potash & Chemical Corporation, Trona, California. (Meeting of the American Chemical Society, Chicago, Illinois, September, 1958).
2. F. Burriel-Martí, J. Ramírez-Muñoz, Flame Photometry A Manual of Methods and Applications, New York, Elsevier Publishing Company, (1957).

IX. ZIRCONIUM IN SODIUM

Abstract

Zirconium is determined colorimetrically with alizarin reagent.

Reagents

Absolute Methanol

1:10 (~1N) Hydrochloric acid

1:1 (~6N) Hydrochloric acid

Ammonium hydroxide

Alizarin solution 0.125 gm. per 100 ml. of deionized water. Warm until the dye has dissolved, cool, and filter.

Procedure

Dissolve the sample in an inert atmosphere by the addition of small pieces to methanol. Add an equal volume of deionized water and heat carefully to evaporate the methanol.

Add an aliquot containing 0.01-0.1 mg. zirconium in about 1:5 hydrochloric acid to a 50 ml. volumetric flask. Add 0.5 ml. of the alizarin solution. Add conc. ammonium hydroxide until the dye-color change indicates that the solution is alkaline. Allow to stand for 2 minutes. Neutralize by adding 1:10 hydrochloric acid dropwise, then add 3 drops of 1:1 hydrochloric acid. Dilute the solution to volume and determine optical density against a reagent blank at or above 560 mμ in a 10 cm Beckman cell. Read ppm zirconium from a calibration curve prepared with standard solutions.

Reference

Snell, F. D., and Snell, C. T., Colorimetric Methods of Analysis, New York, D. Van Nostrand Co., Inc. (1957).

SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN SODIUM

Abstract

Samples are dissolved by the dropwise addition of deionized water under an inert atmosphere, neutralized with hydrochloric acid or sulfuric acid, evaporated, and loaded into craters drilled in graphite electrodes. The electrodes are arced to burn the samples and excite the impurity spectra. Different procedures are used, depending upon the elements sought.

Procedure I-A (General Impurities Except Mercury, Boron, Cadmium, Silicon, Copper, Alkaline Rare Earths).

Sample: Pyrex cups, 1 g. Sodium

Acid: 18N sulfuric acid, then 2N sulfuric acid to the phenolphthalein end point.

Spectrographic: 50 mg., 15 amps, 2 min., Gaertner, 2200-3500 Å

Procedure I-B (Mercury)

Sample: Pyrex cups, 2 samples, 5 g. sodium each.

Acid: 2N hydrochloric acid, titrate to the methyl orange end point + 10 ml. conc. hydrochloric acid.

Spectrographic: Stir with 1 g. copper, Arc copper 30 sec. at 12 amps. DC Gaertner, 2200-3500 Å or Baird 2.7°.

Procedure II (Cadmium, Boron, Silicon, Copper)

Sample: Steel cups, 1 g. sodium

Acid: 18N sulfuric acid, then 2N sulfuric acid to the phenolphthalein end point.

Spectrographic: 75 mg., 15 amps, 2 min., Baird 2.7° plus filters.

Procedure III (Aluminum, Calcium, Strontium, Barium)

Sample and acid same as Procedure II.

Spectrographic: 10 mg. AC arc, Baird 5.2° + filters.

Procedure IV (Rare Earths)

Sample: Steel cups, 5 g. sodium

Acid: 2N HCl, titrate to the methyl orange end point, use Fe^{+++} carrier, precipitate with NH_4^+ etc.

Spectrographic: Solution on flat electrode, Baird, DC arc.

ELEMENTS DETERMINED AND RANGES OF ANALYSIS

<u>Procedure</u>	<u>Element</u>	<u>Range ppm</u>	<u>Spectrographic Limit ppm</u>	<u>Element</u>	<u>Range ppm</u>	<u>Spectrographic Limit ppm</u>
I-A	Beryllium	1-10	-	Molybdenum	2-200	-
	Bismuth	5-50	2	Nickel	1-100	2
	Cobalt	2-100	-	Palladium	2-100	-
	Indium	1-100	-	Silver	2-10	-
	Iron	2-100	5	Thallium	10-100	-
	Lead	5-200	2	Tin	10-200	-
	Magnesium	10-100	10	Titanium	10-200	-
	Manganese	2-50	2	Vanadium	2-200	-
I-B	Mercury	2-200	5			
II	Boron		6	Copper		-
	Cadmium	1-10	-	Silicon		-
III	Aluminum		-	Calcium		400
	Barium		-	Strontium		-
IV	Rare Earths - range varies with different elements, usually 1-10 ppm.					