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ESSENTIAL MATERIAL ANALYTICAL MANUAL

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Prepared by [redacted]

Members of [redacted]
Applied Research Unit, Technical Section
and
Process Units, Manufacturing Department

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PREFACE

Purpose

The purpose of the Essential Material Analytical Manual is to assemble the basic procedures to be used for the analysis of essential materials employed at the Hanford Works. The methods appear in a general form rather than as detailed steps suitable for laboratory use.

The "Specifications Acceptance and Sampling Procedures for Essential Materials" defines the formal essential material specifications and the analyses to be made. The present document defines the corresponding methods of analysis. It replaces the Essential Materials sections of the "Hanford Works Laboratory Manual - 300 Area", HW-12866 and "Hanford Works Laboratory Manual - 200 Areas", HW-12865.

Organization

The summary lists the essential materials to be analyzed in alphabetical form. Sub-headings indicate the specified determinations to be made on each and give reference to the method code.

The methods are assembled on the basis of determinations and are presented in alphabetical form according to the assigned code. In those cases in which a given method is applicable to the determination of the same component or property in more than one essential material, the procedure is broken down and gives reference to each essential material.

The code is based on the following principles. The first letter or pair of letters are the chemical symbol of the element determined. Complex ions are coded according to the key element of the complex, and groups of ions are coded according to the most representative element in the group. Organic compounds are assigned the code letters Zx; physical properties are coded Zy; and miscellaneous instrumental methods, such as spectrographic and gas techniques, are coded Zz.

According to this arrangement, the summary allows quick reference to all essential materials to be analyzed and to all determinations required on each; it also supplies the individual method codes, which serve as a basis for locating the method. Similarly, the arrangement of the written methods permits quick reference to any given analysis.

Additions and Deletions

The analytical methods included are only those for which specifications are established according to the "Specifications Acceptance and Sampling Procedures for Essential Materials". Since it is a function of the Applied Research Unit, Technical Section, to define new methods of analyses and it is the function of the respective Process Unit, Manufacturing Department, to apply the methods, all additions to the manual require prior approval of both units. Methods for the analysis of essential materials not having process application are included in the interest of completeness, even though the entire responsibility lies with the Manufacturing Department in such cases.

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ESSENTIAL MATERIALS ANALYSES

	Method Code
Acenaphthene, Material No. 301	
Melting point	Zy-4
Solubility in chloroform	Zy-11
Alum, Material No. 103	
Aluminum	Al-1
Aluminum Cans, 2A, Material No. 302	
Impurity elements	Zz-21
Aluminum Caps, 2S, Material No. 303	
Impurity elements	Zz-21
Aluminum Ingots, 2S, Material No. 304	
Impurity elements	Zz-21
Aluminum Nitrate	
Assay	Al-1
Water insolubles	Zy-14
Sulfate	S-25
Chloride	Cl-5
Alkali and alkaline earths	Na-2
Heavy metals	Pb-2
Silicon	Si-1
Tin	Sn-1
Iron	Fe-5
Nitrite	N-13
Free nitric acid	H-3
Aluminum-Silicon, Material No. 306	
Silicon	Si-1
Copper	Cu-5
Iron	Fe-5
Aluminum Wafers, 2S, Material No. 305	
Impurity elements	Zz-21
Ammonium Silicofluoride, Material No. 28	
Assay	F-1
Water insolubles	Zy-14
Ammonium Sulfate, Material No. 29	
Assay	S-21
Water insolubles	Zy-14

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	Method Code
Ammonium Sulfite Monohydrate, Material No. 30	
Assay	S-11
Water insolubles	Zy-14
Argon, Material No. 307	
Oxygen	Zz-1
Barium Chloride, Material No. 308	
Water insolubles	Zy-14
Alkali metals as sulfate	Na-1
Strontium and calcium chlorides	Ca-2
Nitrate and chlorate	N-24
Heavy metals	Pb-2
Water	O-2
Bismuth, Material No. 32	
Assay	Bi-1
Nitric acid insolubles	Zy-16
Iron	Fe-5
Sulfur	S-21
Bismuth Subnitrate, Material No. 2	
Assay as the oxide	Bi-1
Chloride	Cl-5
Nitric acid insolubles	Zy-16
Bromobenzene, Material No. 34	
Specific gravity	Zy-10
Boiling range	Zy-3
Color	Zy-1
Bronze, Material No. 309	
Copper	Cu-1
Cadmium	Cd-1 Cd-2
Calcium, Material No. 35	
Free calcium	Ca-1
Oil or grease	Zx-19
Nitrogen	N-3
Chloride	Cl-5
Impurity elements	Zz-21
Calcium Nitrate, Material No. 331	
Assay	Ca-1
Water insolubles	Zy-14
Carbon Dixoide, Material No. 120	
Assay	Zz-1
Oxygen	Zz-1
Carbon monoxide	Zz-1
Hydrogen	Zz-1

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	Method Code
Carbon Tetrachloride, Material No. 310	
Boiling range	Zy-3
Non-volatile residue	Zy-22
Appearance	Zy-1
Ceric Ammonium Nitrate, Material No. 3	
Assay	Ce-1
Chloride	Cl-5
Nitric acid insolubles	Zy-16
Water	O-2
Chromium Nitrate, Material No. 53	
Chromium	Cr-1
Chloride	Cl-5
Iron	Fe-5
Alkali and alkaline earths as sulfates	Na-2
Sulfate	S-21
Ammonia	N-5
Cobalt Nitrate Hexahydrate, Material No. 9	
Assay	Co-1
Chloride	Cl-5
Sulfate	S-21
Iron	Fe-5
Copper	Cu-6
Nickel	Ni-1
Alkali and alkaline earths as sulfates	Na-2
Alkali & Alkaline Earths as Sulfates	Na-2
Copper	Cu-6
Iron	Fe-5
Nickel	Ni-1
Copper, Material No. 311	
Assay	Cu-1
Coal	
Total moisture	C-1
Surface moisture	C-1
Volatile matter	C-1
Fixed carbon	C-1
Ash	C-1
Sulfur	S-21 or Zy-23
Heating value	Zy-23
Ferric Sulfate, Material No. 118	
Assay	Fe-3
Ferrous sulfate	Fe-3
Manganese	Mn-3
Chlorides	Cl-5

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	Method Code
Ferrous Ammonium Sulfate Hexahydrate, Material No. 4	
Assay	Fe-3
Chloride	Cl-5
Water insolubles	Zy-14
Helium, Material No. 36	
Density	Zz 2
Carbon dioxide	Zz-1
Oxygen	Zz-1
Hydrogen	Zz-1
Nitrogen	Zz-1
Water	Zz-3
Hydriodic Acid, Material No. 37	
Assay	H-1
Chloride	Cl-5
Sulfate	S-25
Impurity elements	Zz-21, 22
Hydrogen, Material No. 38	
Oxygen	Zz-1
Water	Zz-3
Hydrofluorosilic Acid, Material No. 312	
Assay	H-1
Non-volatile matter	Zy-22
Chloride	Cl-5
Sulfate	S-25
Heavy Metals	Pb-2
Iron	Fe-5
Hydrogen Peroxide, Material No. 24	
Assay	O-1
Iron	Fe-5
Hydrogen Peroxide, Material No. 32	
Assay	O-1
Impurity elements	Zz-21
Iodine, Material No. 44	
Chlorine and bromine	Cl-6
Non-volatile matter	Zy-22
Iron Powder, Material No. 13	
Particle size	Zy-24
Lanthanum Ammonium Nitrate, Material No. 7	
Lanthanum	La-1
Nitric acid insolubles	Zy-16
Chloride	Cl-5

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	Method Code
Lime, Material No. 108	
Calcium oxide	Ca-1
Particle size	Zy-24
Manganous Nitrate, Material No. 8	
Assay	Mn-1
Chloride	Cl-5
R_2O_3	Fe-1
Magnesium Oxide, Material No. 40	
Silica	Si-1
R_2O_3	Fe-1
Calcium oxide	Ca-1
Particle size	Zy-24
Impurity elements	Zz-21
Methanol, Material No. 314	
Specific gravity	Zy-10
Boiling range	Zy-2
Non-volatile residue	Zy-22
Color	Zy-1
Odor	Zy-8
Acidity	H-2
Methyl Isobutyl Ketone, Material No. 27	
Boiling range	Zy-3
Refractive index	Zy-5
Color	Zy-1
Acidity	H-2
Mesityl oxide	Zx-7
Oxidizing impurities	Zy-20
Metso "99", Material No. 333	
Water insolubles	Zy-14
Boron	Zz-22
Naccanol, Material No. 334	
Water insolubles	Zy-14
Boron	Zz-22
Nitric Acid, 60%, Material No. 10	
Assay	H-1
Nitric oxides	N-11
Chloride	Cl-5
Non-volatile residue	Zy-22

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	Method Code
Nitric Acid, 70%, Material No. 41	
Assay	H-1
Chloride	Cl-5
Sulfate	S-25
Arsenic	As-1
Iron	Fe-5
Nitric oxides	N-11
Heavy metals	Pb-2
Non-volatile residue	Zy-22
Impurities	Zz-21, 22
Nitric Acid, 95%, Material No. 52	
Assay	H-1
Nitric oxides	N-11
Non-volatile residue	Zy-22
Ether extractables	Zy-13
Iron	Fe-5
Chromium	Cr-3
Nitrogen, Material No. 45	
Oxygen	Zz-1
Water	Zz-3
Carbon dioxide	Zz-1
Oxalic Acid Dihydrate, Material No. 11	
Assay	Zx-3
Water insolubles	Zy-14
R_2O_3	Fe-1
Chloride	Cl-5
Oxalic Acid Dihydrate, Material No. 42	
Assay	Zx-3
Chloride	Cl-5
Iron	Fe-5
Heavy metals	Pb-9
Water insolubles	Zy-14
Nitrogen compounds	N-5
Non-volatile residue	Zy-22
Sulfate	S-25
Impurities	Zz-21, 22
Oxygen, Material No. 43	
Hydrogen	Zz-1
Water	Zz-3

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	Method Code
Petroleum Diluent, Material No. 46	
Viscosity	Zy-9
Flash point	Zy-6
Olefins	Zx-21
Aromatics	Zx-9
Specific gravity	Zy-10
Phosphoric Acid, Material No. 317	
Assay	H-1
Chloride	Cl-5
Iron	Fe-5
Sulfate	S-25
Alkali metals as sulfates	Na-1
Phosphoric Acid, Material No. 12	
Assay	H-1
Chloride	Cl-5
Iron	Fe-5
Reducing materials	Zy-21
"P" Lead Dummies, Material No. 107	
Cadmium	Cd-5
Potassium Chloride, Material No. 316	
Insolubles	Zy-14
Neutrality	H-21
Chlorate and nitrate	N-24
Nitrogen compounds	N-5
Phosphate	P-1
Sulfur compounds as sulfate	S-25
Water	O-2
Alkali, alkaline earths, and ammonium hydroxide precipitate	Ca-3
Potassium Hydroxide, Material No. 14	
Total alkalinity as potassium oxide	H-13
Carbonate as potassium carbonate	H-13
Iron	Fe-5
Chloride	Cl-5
Water insolubles	Zy-14
Potassium Permanganate, Material No. 26	
Assay	Mn-1
Water insolubles	Zy-14
Silver Nitrate, Material No. 47	
Assay	Ag-1
Chloride	Cl-5
Hydrochloric acid solubles	Zy-~~18~~ 17

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	Method Code
Sodium Bicarbonate, Material No. 31	
Assay	H-11
Sodium Bismuthate, Material No. 15	
Assay	Bi-3
Chloride	Cl-5
Water insolubles	Zy-14
Particle size	Zy-24
Sodium Carbonate, Material No. 16	
Sodium oxide	H-11
Water insolubles	Zy-14
Sodium Chloride (Rock Salt), Material No. 110	
Assay	Cl-1
Water insoluble	Zy-14
Sodium Chloride, Material No. 318	
Nitrogen compounds	N-5
Phosphate	P-1
Sulfate	S-25
Water	O-2
Ammonium hydroxide precipitate	Ca-3
Water insolubles	Zy-14
Neutrality	H-21
Chlorate and nitrate	N-24
Sodium Dichromate Dihydrate, Material No. 112	
Assay	Cr-1
Water insolubles	Zy-14
Sodium Dichromate Dihydrate, Material No. 17	
Assay	Cr-1
Water insolubles	Zy-14
Sulfate	S-21
Sodium Hydroxide, Material No. 19	
Sodium oxide	H-11
Sodium hydroxide	H-11
Sodium chloride	Cl-5
Sodium Hydroxide, Material No. 54	
Total alkalinity as sodium oxide	H-11
Sodium carbonate	H-11
Iron	Fe-5
Chloride	Cl-5
Water insolubles	Zy-14

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	Method Code
Sodium Nitrate, Material No. 22	
Water insolubles	Zy-14
Nitrate	N-21
Chloride	Cl-5
Sulfate	S-21
Sodium Nitrite, Material No. 23	
Assay	N-10
Water	O-2
Water insolubles	Zy-14
Sodium Pyrophosphate, Material No. 320	
Assay	P-11
Water insolubles	Zy-14
Sodium Silicate (Aqueous), Material No. 113	
Sodium oxide	H-11
Silica	Si-5
Sodium Sulfate, Material No. 48	
Assay	S-21
Sodium chloride	Cl-5
Sodium Sulfite, Material No. 114	
Assay	S-11
Sodium Sulfate	S-21
Water insolubles	Zy-14
Sulfamic Acid, Material No. 49	
Chloride	Cl-5
Nitrate	N-23
Silica	Si-1
Tin	Sn-1
Heavy metals	Pb-2
Sulfuric Acid, Material No. 20	
Assay	H-1
Iron	Fe-5
Organic matter	Zx-1
Nitric acid and oxides of nitrogen	N-21
Super Filtrol, Material No. 50	
Particle size	Zy-24
Tin, Material No. 322	
Cadmium	Cd-1
Sulfur	S-23

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	Method Code
Tributylphosphate, Material No. 51	
Butanol	Zx-5
Acidity	H-2
Suspended solids	Zy-15
Specific gravity	Zy-10
Water	O-3
Trichloroethylene, Material No. 323	
Boiling range	Zy-3
Total alkalinity	H-12
Non-volatile residue	Zy-22
Chloride	Cl-5
Water	O-3
Zirconium Carbonate Gel, Material No. 21	
Zirconium oxide	Zr-1
Chloride	Cl-5
Nitric acid insoluble	Zy-16

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DETERMINATION OF SILVER

Gravimetric Method

Principle

Silver ion reacts with HCl to form insoluble silver chloride, a suitable salt for gravimetric analysis. Antimony, lead, and mercury will also be precipitated, if present.

Procedure - Analysis of Silver Nitrate

Weigh accurately 1 g. of sample, dissolve in about 100 ml. of water, and heat to boiling. Add dropwise, with stirring, 5 ml. of 2 N HCl. Let stand for a few minutes, then decant the solution into a Selas curcible, and test the filtrate with a drop of dilute HCl to make sure all the silver is precipitated. Wash three times by decantation, using hot 1% HNO_3. Transfer the precipitate to the crucible and wash until free from chlorides, about six to eight additional washings being sufficient. Wash once with alcohol and dry at 110°C to constant weight.

Calculations

$$\% \; AgNO_3 = \frac{\text{g. } AgCl \times 118.52}{\text{g. sample}}$$

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand Co., Inc., New York, 821 (1939)(5th Ed.).

Written by: L. F. Kendall
Date: July, 1952

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DETERMINATION OF ALUMINUM

8-Hydroxyquinoline Method

Principle

8-Hydroxyquinoline precipitates aluminum quantitatively from a weak acid solution. A large number of other cations are also precipitated by this reagent. Interference by some of them, such as Mg, Ca, Ba, can be eliminated by carrying out the precipitation in a buffered acetic acid solution. However, other common ions, such as iron, nickel, copper, zinc, etc., precipitate under the same conditions and can best be removed by electrolysis at a mercury cathode. For the analyses indicated below, no interferences are normally expected. The procedure is generally applicable for 0.2-50 mg. of aluminum. Larger quantities give high results because of adsorption of excess precipitant. The precipitate forms according to the following reaction:

$$Al^{+++} + 3HOC_9H_6N \longrightarrow Al(OC_9H_6N)_3\downarrow + 3H^+$$

Solutions

8-Hydroxyquinoline, 5%. Dissolve 50 g. of 8-hydroxyquinoline in 120 ml. of glacial acetic acid and dilute to 1 liter with water. Filter if necessary and store in a dark bottle.

Procedure - Analysis of Alum

Weigh 0.4-0.55 g. of the sample. Dissolve in 200 ml. of water and continue as in general procedure.

Procedure - Analysis of Aluminum Nitrate Solution

Weigh a 10 g. sample and transfer quantitatively to a 250 ml. volumetric flask, dilute to volume and mix. Pipet a 10 ml. aliquot into a beaker and adjust volume to 100 ml., then proceed as indicated below.

Procedure - General

Adjust pH of sample to 4 with 1:1 NH_4OH. Add sufficient 5% 8-hydroxyquinoline to precipitate the aluminum. One ml. of the solution will precipitate 3 mg. of aluminum; an excess of 15-25% should be used. Heat to 60-70°C, add 4 $\underline{M}$ ammonium acetate dropwise until the yellow color deepens, then add 5 ml. additional for each 100 ml. of solution. The pH should now be between 5.0 and 5.4. Stir well and allow to stand 4 hrs. at room temperature.

Filter through a tared, sintered glass or Selas crucible and wash with cold water. Dry for 2 hrs. in an oven at 135-140°C. Cool in a desiccator and weigh.

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Calculations

$$\% \ Al_2O_3 \text{ in alum} = \frac{\text{g. residue} \times 0.111 \times 100}{\text{g. sample}}$$

$$\% \ ANN = \frac{\text{g. residue} \times 0.8165 \times 100}{\text{g. sample in aliquot}}$$

References

1. Furman, N. H., "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand, New York (1939), p. 12.

2. Mellan, I., "Organic Reagent in Inorganic Analysis", The Blakiston Co., Philadelphia (1941), pp. 119-129 and 239-244.

3. Welcher, F. J., "Organic Analytical Reagents", D. Van Nostrand Co., Inc., New York (1947) Vol. 1, pp. 285-292.

Written by: G. B. Barton
Date: July, 1952

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DETERMINATION OF ARSENIC

Gutzeit Method

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Principle

Arsine is evolved from arsenic compounds by nascent hydrogen in the presence of zinc catalyst. The arsine reacts with mercuric chloride paper to form a colored compound. From the length and intensity of the color stain, the amount of arsenic is estimated by comparison with standard stains. Interfering substances are nitric acid, halogens, hydrogen sulfide, sulfur dioxide, phosphine, and $>$0.1 mg. of antimony. The apparatus has a trap for the removal of traces of hydrogen sulfide. The arsenic should be separated from quantities greater than 0.1 mg. of antimony by distillation. The method is accurate for determining arsenic in amounts ranging from 0.001-0.02 mg. As_2O_3.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2H$$

$$As_2O_3 + 12H \xrightarrow{Zn} 2AsH_3 + 3H_2O$$

$$2AsH_3 + 3HgCl_2 + 4O_2 \longrightarrow Hg_3(AsO_4)_2 + 6HCl$$

Apparatus

Small Gutzeit apparatus. See diagram.

Solutions

Standard arsenic solution, 1 mg. arsenic per ml. Dissolve 1.3203 g. of resublimed arseneous oxide in 25 ml. of 20% arsenic-free sodium hydroxide. Neutralize with 4 N sulfuric acid and transfer solution to a 1000 ml. volumetric flask. Dilute to the mark and mix.

Dilute standard arsenic solution, .001 mg/ml. Pipet 1 ml. of standard arsenic solution containing 1 g/1 of arsenic into a 1 liter volumetric flask and dilute to the mark with 4 N sulfuric acid.

Stannous chloride solution, 40%. Dissolve 40 g. of stannous chloride in 100 ml. of water containing 5 ml. of arsenic-free concentrated hydrochloric acid.

Lead acetate solution, 10%. Dissolve 10 g. of lead acetate in 100 ml. of water containing a sufficient amount of acetic acid to keep the solution clear.

Lead acetate paper. Soak a qualitative filter paper in the 10% lead acetate solution, dry, cut into 7 cm x 5 cm strips, and store in an air-tight bottle.

Sensitized mercuric chloride paper. Dip a 20 cm circle of O.K. Swedish filter paper into a 0.35% mercuric chloride solution and dry in a vertical position in air free of fumes. Cut into 12 cm x 2.5 mm. strips and store in an air-tight bottle. Paper with a white deposit of mercuric chloride should not be used.

Zinc. Treat arsenic-free zinc shot, 3-6" mesh, with concentrated hydrochloric acid until the surface is clean and dull. Wash with water and store under water.

July, 1952

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Procedure - Analysis of Nitric Acid

Evaporate a weighed 100 g. sample with 5 ml. of concentrated H_2SO_4 to SO_3 fumes. Transfer the solution to the Gutzeit generator bottle and determine the arsenic following the general procedure.

Procedure - Analysis of Phosphoric Acid

Place a weighed 1.5 g. sample in a distilling flask connected with a coil condenser to the Gutzeit generator bottle containing 20-30 ml. of cold water. Add 50 ml. of arsenic-free concentrated hydrochloric acid and 5 g. of cuprous chloride to the sample. Heat to boiling and pass a current of air through strong hydrochloric acid into the distilling flask. The arsenic contained in the first 10-15 ml. of distillate is determined following the general procedure.

Procedure - General

Add 5 ml. of arsenic-free concentrated hydrochloric acid (Remark 1), 7.5 ml. of 10% potassium iodide, and 4 drops of the stannous chloride solution to the sample in the Gutzeit generator bottle. Allow to stand 30 min. at 25°C and dilute to 40 ml. total volume. Add 2-5 g. of granulated zinc and immediately connect the generating bottle to the tube assembly, which has been previously prepared as shown in the diagram (Remark 2). Keep the bottle immersed in the water bath at 25°C for 1.5 hr.

Remove the test strip and dip in molten paraffin. The amount of arsenic should not exceed that of a standard stain which is produced by carrying 3 ml. of the dilute standard arsenic solution through the procedure in place of the sample (Remark 3).

Remarks

1. Identical conditions, such as acidity, amount of zinc, temperature, time, size of strips, etc., must be maintained for all samples and standard stains.

2. Prepare the testing assembly by inserting a dry sheet of lead acetate paper in the lower part of tube B, as shown in figure. Place a small roll of glass wool moistened with lead acetate in the upper part of tube B, as shown in the figure. Insert a strip of sensitized mercuric chloride paper in tube A and connect to the lower tube, as shown in the figure.

3. Standard stains should be prepared each time to eliminate any errors introduced by new reagents. Blanks should be run on the reagents to determine if any of the reagents contain arsenic in amounts greater than the standard. If the latter is the case, prepare new reagents.

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Page As-1-3

References

1. "Reagent Chemicals", A.C.S. Specifications, American Chemical Society, Washington, D.C., pp. 3-5 (1950).

Written by: M. M. Jones
Date: July, 1952

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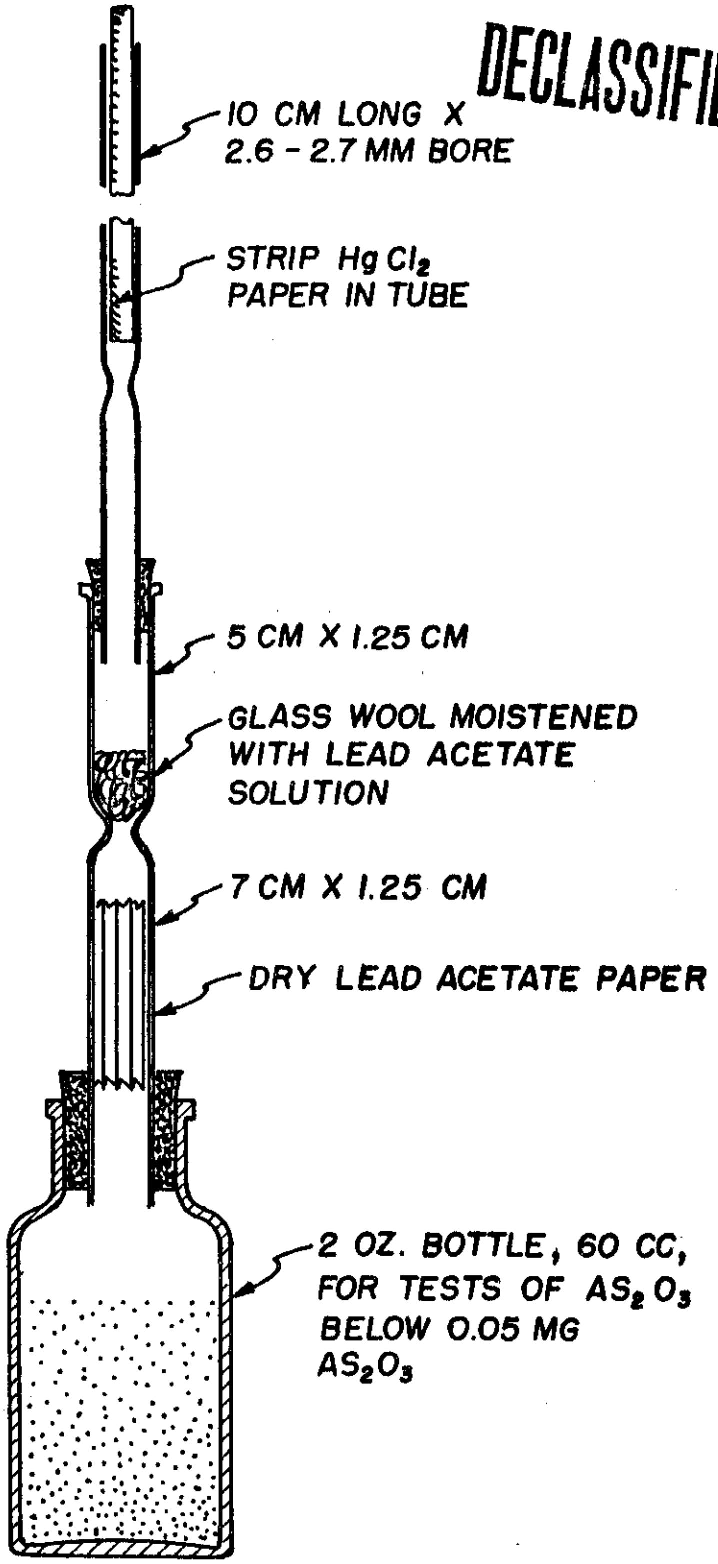

SMALL GUTZEIT APPARATUS
FOR ARSENIC DETERMINATION

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Page Bi-1-1

DETERMINATION OF BISMUTH

Gravimetric Method

Principle

In the absence of acids, bismuth salts hydrolyze to form basic compounds. In this determination bismuth is precipitated as the basic carbonate, which is ignited and weighed as Bi_2O_3. Calcium, barium, lead, hydrochloric, and sulfuric acids interfere.

$$Bi + 4HNO_3 \longrightarrow Bi(NO_3)_3 + NO + 2H_2O$$
$$BiONO_3 + 2HNO_3 \longrightarrow Bi(NO_3)_3 + H_2O$$
$$2Bi(NO_3)_3 + (NH_4)_2CO_3 + 2H_2O \longrightarrow Bi_2O_3 \cdot CO_2 \cdot H_2O + 2NH_4NO_3 + 4HNO_3$$
$$Bi_2O_3\ CO_2\ H_2O + HEAT \longrightarrow Bi_2O_3 + CO_2 + H_2O$$

Procedure - Analysis of Bismuth

Dissolve 0.20 to 0.25 g. of accurately weighed sample in 5 ml. of concentrated nitric acid. Boil for a few minutes to insure complete dissolution. Cool, and dilute to 300 ml.

Add concentrated ammonium hydroxide until slightly milky. Add saturated ammonium carbonate solution until precipitation ceases. Continue as under "General".

Procedure - Analysis of Bismuth Subnitrate

Dissolve a 1 g. accurately weighed sample in 20 ml. of hot 4 N nitric acid. Dilute to 250 ml. Add saturated ammonium carbonate solution until precipitation ceases. Continue as under "General".

Procedure - General

When no more precipitate forms, boil for a few minutes and digest on steam bath for 2 hrs. Filter through a tared 3010 Selas crucible or Gooch crucible containing an asbestos mat. Wash three times with hot distilled water. Dry in a 105°C oven. Ignite in muffle furnace at 650°C to constant weight.

Calculations

$$\% \text{ Bi} = \frac{\text{g. ppt.} \times 0.8970 \times 100}{\text{g. sample}}$$

References

1. Furman, "Scott's Standard Methods of Chemical Analysis", Vol. I, D. Van Nostrand Co., Inc., 155 (1939).

July, 1952

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2. Hillebrand and Lundell, "Applied Inorganic Analysis", John Wiley and Sons, 190, (1929).

3. Treadwell and Hall, "Analytical Chemistry", John Wiley and Sons, 64 (1942).

Written by: R. Ko
Date: July, 1952

[redacted]

[redacted]

[redacted]

Code Bi-3

DETERMINATION OF BISMUTH

Volumetric Method

DECLASSIFIED

Principle

Sodium bismuthate is determined by measuring the oxidizing power of a sample. The presence of other oxidants will give erroneous results.

$$2NaBiO_3 + 4FeSO_4 + 3H_2SO_4 \longrightarrow Bi_2(SO_4)_3 + 2Fe_2(SO_4)_3 + Na_2SO_4 + 6H_2O$$

Solutions

Standardized ceric sulfate, 0.1 N.

Ferrous sulfate: dissolve 7 g. of ferrous sulfate in 90 ml. of freshly boiled and cooled water. Add conc. sulfuric acid to make 100 ml. This solution must be freshly prepared as required.

Ferroin indicator, 0.025 M.

Procedure - Analysis of Sodium Bismuthate

Weigh accurately 0.7 g. of sample, place in a flask, and add 25.0 ml. of ferrous sulfate solution. Stopper the flask, let stand half an hour with frequent shaking, and titrate the excess ferrous sulfate with 0.1 N ceric sulfate solution, using ferroin indicator. Titrate also 25.0 ml. of ferrous sulfate solution.

Calculations

$$\%\ NaBiO_3 = \frac{V \times N \times 14.00}{\text{g. sample}}$$

V = ml. of ceric sulfate for blank - ml. for sample
N = normality of ceric sulfate

Literature References

1. Hillebrand and Lundell, "Applied Inorganic Analysis", John Wiley and Sons, New York, 35 (1929).

2. "Reagent Chemicals, ACS Specifications", American Chemical Society, Washington, 311 (1950).

Written by: L. F. Kendall
Date: July, 1952

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Page C-1-1

ANALYSIS OF COAL

DETERMINATION OF WATER, ASH, VOLATILE MATTER, AND FIXED CARBON

Gravimetric Method

Principle

The determinations are made by heating the sample under carefully controlled conditions, each peculiar to the item being determined.

The water determination is composed of three determinations; namely, air-dried moisture which is obtained by drying the sample "as received" at 80-90°F to constant weight, moisture in air-dried sample which is obtained by heating a portion of pulverized sample at 105°C for 1 hr., and the total moisture which is calculated from the two previous determinations. The weighings must be made as soon as possible in all cases to eliminate errors due to loss of water from wet samples and absorption of water by the pulverized sample.

Mechanical losses are the main source of error in the determination ofvolatile matter and are caused by the rapid escape of the volatile matter, particularly when sub-bituminous coal is heated suddenly. These fuels should be heated gradually, beginning at a low temperature to avoid this error.

Rapid expulsion of the volatile matter frequently entrains some of the ash causing low results. This error in the ash determination is eliminated by giving careful attention to the conditions of ignition.

Fixed carbon in coal is defined as the difference between 100% and the sum of the percents moisture, volatile matter, and ash.

Procedure - Determination of Water.

Fill a tared No. 6 porcelain dish with sample and weigh. Dry in an oven at 80-90°F until the loss in weight between two successive weighings, 6-12 hrs. apart, does not exceed 0.1% per hr. Treat the sample container in the same manner to determine a blank.

Immediately after the last weighing pulverize a portion of the sample to 60 mesh by mechanical means and store the remaining sample in a stoppered bottle. Collect 50 g. of 60 mesh material using the riffle sampler and store in a stoppered bottle.

Weigh accurately 1 g. of 60 mesh sample and 5 g. of 200 mesh sample into evaporating dishes. Heat in an oven at 105°C for 1 hr. Cool to room temperature and weigh.

Procedure - Determination of Ash

Weigh accurately 1 g. of the 60 mesh air-dried sample into tared ash capsule. Heat at 150-200°C until the volatile matter is driven off. Ignite at 700-750°C for 2 hrs. Cool to room temperature and weigh.

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Procedure - Determination of Volatile Matter

Weigh accurately 1 g. of the 60 mesh air-dried sample into a tared 15 ml. platinum crucible. With cover in place, preheat the sample for not less than 5 min., and not more than 10 min. in the preheater of the Fieldner furnace. After preheating, place in full heat of the furnace for exactly 6 min. at 950°C. Cool to room temperature and weigh (Remark 1).

Procedure - Determination of Fixed Carbon

Obtained by calculation.

Calculations

A. Water

$$\% A = \frac{\text{g. loss(at 80-90°F)}}{\text{g. sample}} \times 100$$

$$\% S = \frac{\text{g. loss(at 105°C)}}{\text{g. sample}} \times 100$$

$$\% M = \frac{100 - A}{100} \times S + A$$

A = % air-dry moisture
S = % moisture in 60 mesh coal
M = % total moisture of sample "as received".

B. Ash

$$\%\ \text{ash "as received"} = \frac{\text{g. ash} \times 100}{\text{g. sample}} \times \frac{(100 - A)}{100}$$

C. Volatile matter

$$\%\ \text{volatile matter "as received"} = \frac{\text{g. loss(at 950°)} \times 100}{\text{g. of sample}} \times \frac{100 - A}{100}$$

D. Fixed carbon

100.00 - (% M + % volatile matter + % ash).

Remarks

1. If sparking is observed during any portion of the heating period, reject the determination and repeat.

References

1. Bureau of Mines Technical Paper No. 8, 1938, "Method of Analyzing Coal and Coke".

Written by: R. E. Ewing
Date: July, 1952

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DETERMINATION OF CALCIUM

Gravimetric Method

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Principle

The determination of free calcium metal is carried out by ignition of the sample in air to the oxide. The gain in weight is used to calculate free calcium.

The determination of total calcium is accomplished by precipitation as the oxalate from a slightly ammoniacal solution or oxalate-oxalic acid buffered solution of the salts. The precipitate is ignited to calcium oxide for weighing. Other alkaline earths, ferric iron and aluminum, manganese and some of the rare earths may interfere. To avoid contamination of the calcium precipitate by Mg, Sr, and Ba, a double precipitation is desirable, particularly in the presence of large amounts of Mg. The presence of NH_4Cl hinders the precipitation of Mg. The remainder of the interfering elements if present in appreciable amounts, are removed prior to analysis by hydroxide precipitation. The precipitation from an oxalate-oxalic acid buffered solution enables direct separation from small amounts of these elements.

Procedure - Analysis of Calcium for Free Calcium

Weigh a one gram sample into a covered platinum dish, and cautiously add 30 to 40 ml. of distilled water (in hood). After the sample has cooled, wash the platinum covers, and then evaporate the sample to dryness on a hot plate. Ignite to constant weight at 1200°C, cool in a desiccator, and weigh (covered).

Procedure - Analysis of Calcium for Total Calcium

Cautiously dissolve a 0.5 g. sample in about 100 ml. of distilled water. When the reaction has subsided, add at least 5 ml. of concentrated HCl to dissolve the calcium hydroxide. Then neutralize with NH_4OH, warm the solution, add 15 ml. of concentrated oxalic acid, and add 100 ml. of saturated ammonium oxalate solution slowly and with constant stirring. Continue according to the general procedure below.

Procedure - Analysis of Lime

Dissolve a 2 g. sample with 50 ml. of H_2O and 15 ml. of HCl, add about 1 ml. of HNO_3 and boil for 5 minutes. Neutralize with NH_4OH and add a slight excess, digest at the boiling point until the odor of ammonia is barely preceptible, let the precipitate settle well, and filter through Whatman #41 filter paper. Wash thoroughly with hot water, combine washings and filtrate, and dilute to 250 ml. (Remark 1). Take a 50 ml. aliquot for analysis. Heat the 50 ml. aliquot to boiling, add 75 ml. of 4% ammonium oxalate solution slowly and with continuous stirring. Continue according to the general procedure.

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Procedure - Analysis of Magnesium Oxide

Weigh a 1 g. sample into a platinum crucible, add about 6 times as much Na_2CO_3, and mix thoroughly. Cover the crucible and cautiously bring the contents to the melting point, continuing the fusion until the melt is clear and homogeneous.

Cool the crucible, rotating it so the melt solidifies on the sides in a thin layer, immerse in a beaker of water and heat until the solid is dissolved. Carefully add 20 ml. of 70% perchloric acid to the solution, cover with a watch glass, and evaporate to fumes of $HClO_4$. Boil for 10 or 15 minutes after the fuming point (Remark 2), cool and dilute about 1 to 5. Heat to boiling, filter and wash with 1:100 HCl solution (Remark 3).

Dilute the combined filtrate and washings to 250 ml., take a 25 ml. aliquot for analysis, dilute it to approximately 100 ml., and neutralize with NH_4OH. Acidify the sample with concentrated oxalic acid, add a 10 ml. excess, and then add 20 ml. of saturated ammonium oxalate slowly and with continuous stirring.

Digest, filter and wash the precipitate according to the general procedure, and then instead of igniting, dissolve the precipitate in 50 ml. of HCl. Neutralize with ammonium hydroxide, acidify with concentrated oxalic acid, and carry out the precipitation again in the same manner as above. Continue according to the general procedure.

Procedure - General

After the addition of ammonium oxalate is complete, allow the solution to digest for one hour on a steam bath, then filter through an ashless type medium filter paper (Whatman #42), and wash with water containing 2 g/l of ammonium oxalate.

Transfer the precipitate to a tared platinum crucible, dry, and ignite at about 1200°C till constant weight is obtained. Cool in a desiccator and weigh with a lid on the crucible.

Calculations

$$\% \text{ free Ca} = \frac{(\text{g. residue} - \text{g. sample}) \times 2.505 \times 100}{\text{g. sample}}$$

$$\% \text{ total Ca} = \frac{\text{g. precipitate} \times 0.7147 \times 100}{\text{g. sample in aliquot}}$$

or

$$\% \text{ total CaO} = \frac{\text{g. ignited precipitate} \times 100}{\text{g. sample in aliquot}}$$

Remarks

1. In the determination of calcium in lime, this pretreatment is provided to remove Si, Fe, Al, and Mn. The washings and filtrate from the determination of R_2O_3 in the sample may be taken for the sample. Dilute these

to 250 ml., take a 50 ml. aliquot, and continue, omitting the initial NH_4OH precipitation step outlined here.

2. Do not allow the contents of the beaker to become solid.

3. In the determination of CaO in MgO this pretreatment is provided to remove silica. Instead of this step, the filtrate and washings from the determination of silica in the MgO sample may be taken and used at this point. Dilute to 250 ml., take a 25 ml. aliquot and continue as outlined above.

4. The ignited CaO must be weighed quickly since it will pick up moisture from the air. The desiccator must contain a better disiccant than CaO. $CaCl_2$ is not satisfactory.

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand, Co., Vol. 1, p. 210 (1939).

2. Ibid., p. 214.

3. Griffin, "Technical Methods of Analysis", 2nd Ed., p. 428.

Written by: R. J. Brouns
Date: July, 1952

[redacted]

DETERMINATION OF STRONTIUM AND CALCIUM

Gravimetric Method

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Principle

The chlorides of strontium and calcium are soluble in alcohol while barium chloride is insoluble.

Procedure - Analysis of Barium Chloride

Contact 2.000 g. of the finely powdered sample with 20 ml. of absolute alcohol in a 200 ml. erlenmeyer flask for 30 minutes with occasional shaking. Decant the alcohol solution through a dry Whatman No. 40 filter paper and evaporate the filtrate to dryness in a tared porcelain crucible which has been ignited to constant weight at 600°C. Ignite the residue at about 600°C and weigh.

Calculations

$$\% \ SrCl_2 \text{ plus } CaCl_2 = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

Literature References

1. "Specifications for Analytical Reagents", American Chemical Society, Washington, D.C., p. 35 (March, 1941).

Written by: R. J. Brouns
Date: July, 1952

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DETERMINATION OF CALCIUM, MAGNESIUM, AND AMMONIUM HYDROXIDE PRECIPITATE

Gravimetric Method

Principle

Elements which form an insoluble hydroxide are precipitated by the addition of an excess of ammonium hydroxide. This includes elements such as iron, chromium, and aluminum. The hydroxides of calcium and magnesium are somewhat soluble and these are precipitated as the oxalate and phosphate, respectively.

Procedure - Analysis of Potassium Chloride and Sodium Chloride

Dissolve 20 g. sample in 200 ml. of warm water, allow to stand on a steam bath for one hr. and filter without washing. To the filtrate add 5 ml. of ammonium oxalate (35 g. $(NH_4)_2C_2O_4 \cdot H_2O$/l.), 2 ml. of ammonium phosphate (130 g. $(NH_4)_2HPO_4$/l.), and 30 ml. of C.P. Ammonium hydroxide. Allow to stand overnight. Filter the precipitate through a Whatman No. 42 filter paper, wash with water containing 2.5% ammonia, ignite in a tared platinum crucible, and weigh.

Calculations

$$\% \text{ insoluble} = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

References

1. A.C.S., "Reagent Chemicals, A.C.S. Specifications", 1950, pp.258-324.

Written by: H. R. Schmidt
Date: July, 1952

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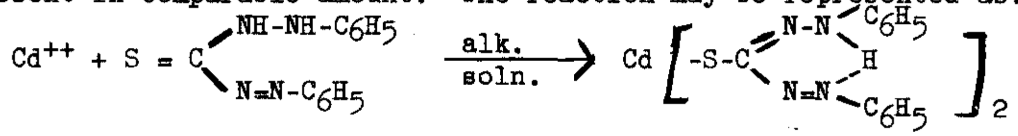
DETERMINATION OF CADMIUM

Dithizone Method, Colorimetric

Principle

Small amounts of cadmium can be extracted from bivalent tin as the dithizonate in an alkaline solution. The tin is reduced to stannous state with hydroxylamine hydrochloride. Interference from lead, zinc, and bismuth is negligible in highly alkaline solution, and interference from copper, silver, and mercury is not great for moderate amounts of these elements. Nickel can interfere if present in comparable amount. The reaction may be represented as:



The color is somewhat unstable, but satisfactory results are obtained for the cadmium concentrations normally present in tin samples.

Solutions

Dithizone solution, 5 mg./l. The reagent (Diphenylthiocarbazene, E.K.No. 3092) should first be purified as follows. Dissolve 1 g. dithizone in 50-75 ml. purified chloroform in a separatory funnel. Extract with four 100 ml. portions of 3% NH_4OH. Make combined aqueous phases slightly acid with HCl and extract the re-precipitated dithizone with 75 ml. chloroform. Wash the organic solution with several portions of re-distilled water, discarding the aqueous wash. Evaporate the organic solution to dryness on a steam bath in hood. Dry in vacuum at 50°C for at least one hour. Store in amber bottle in cool place.

Prepare a solution of 5 mg./l. dithizone in chloroform, adding 10 ml. absolute ethanol per liter to enhance stability. Store in amber bottle in refrigerator.

Cadmium standard, 0.1 g./l. Dissolve 0.1631 g. anhydrous $CdCl_2$, or 0.1951 g. $CdCl_2 \cdot 2H_2O$ in water and dilute to one liter.

Procedure - Analysis of Tin

Accurately weigh 5 g. sample and dissolve in about 30 ml. concentrated nitric acid. Evaporate to dryness on steam bath, and then bake on hot plate. Redissolve residue in 25 ml. re-distilled water and 1 ml. nitric acid, digesting on steam bath 5-10 min. Filter (double paper, partly filled with pulp) and wash filter well with distilled water.

Neutralize the combined filtrate and washings with ammonium hydroxide. Add 10 ml. of 10% hydroxylamine hydrochloride and adjust pH to 11-12 with NaOH.

Transfer the sample to a separatory funnel and extract with three 5 ml. portions of dithizone solution, shaking about one minute for each extraction. Collect the dithizone (bottom) fractions in a 50 ml. Nessler tube and dilute to 50 ml. with chloroform.

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Similarly, prepare color standards (Remark 1), using 1 ml. standard cadmium solution (0.1 g./l.) and such fractions or multiples of this volume as necessary to match the sample (Remark 2). Express the sample in terms of equivalent volume of standard solution.

Calculations

$$\% \text{ Cd} = \frac{\text{equiv. ml. Cd soln.}}{100 \times \text{g. sample}}$$

Remarks

1. Start color standard preparation with ammonia neutralization step, prior to addition of hydroxylamine hydrochloride. Standards must be freshly prepared.
2. Compare visually, or for greater precision, on the spectrophotometer.
3. The above procedure is based on those given in the reference but assumes much lesser amounts of interfering metals to be present.

Literature References

1. Sandell, E. B., "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience, pp. 227-238 (1950).

Written by: U. L. Upson
Date: July, 1952

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DETERMINATION OF CADMIUM

Flame Photometric Method

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Principle

Solutions containing cadmium in sufficient concentration give rise to the characteristic emission spectrum of cadmium when aspirated into a hydrogen-oxygen flame. The intensity of light emitted by cadmium at 326.2 mu is nearly proportional to the cadmium concentration over the range 1-2 g/l cadmium. The cadmium concentration in a solution containing an unknown amount of cadmium may be determined by measuring the emission at 326.2 mu and comparing with standard cadmium solutions.

Lead present at a concentration several times that of the cadmium causes a positive error in the determination. If the same amount of lead is present in the standard solutions, the error is eliminated. Nitric acid may be present in concentrations up to 100 g/l without causing deviations in the emission by cadmium.

Apparatus

Beckman Model DU Spectrophotometer
Beckman Flame Accessory #9200
Beckman Photomultiplier Attachment #4300.

Solutions

Cd, 15 g/l. Weigh out 7.50 g. Cd metal. Cover with about 75 ml. of water and add 15 ml. of concentrated HNO_3 at a rate sufficient to maintain a rapid dissolution of the metal. When all of the nitric acid has been added, it may be necessary to heat the solution to dissolve the remaining metal. When the metal has completely dissolved, transfer to a 500 ml. volumetric flask, cool, and dilute to volume with distilled water. The solution contains 15 g/l Cd and 13 g/l excess HNO_3.

Procedure - Analysis of Cd-Pb Alloy

Prepare a standard calibration curve for cadmium-lead solutions in the following manner: pipet 25 ml. of a 310 g/l $Pb(NO_3)_2$ solution and 8.3 ml. of concentrated HNO_3 into each of eight 100 ml. volumetric flasks. Pipet 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, and 14.0 ml. of the 15 g/l Cd solution into the flasks. Dilute to 100 ml. with distilled water. The solutions contain 1.05, 1.20, 1.35, 1.50, 1.65, 1.80, 1.95, and 2.10 g/l Cd, respectively. (Remark 1)

Measure the emission of Cd in the solutions with the flame photometer. Set the wave length at 326.2 mu, the sensitivity control near the counterclockwise limit, the selector switch at 0.1, and the transmission dial near 80%. With the 2.10 g/l Cd solution aspirating, adjust the slit width to obtain an on-scale reading of the indicator needle. Make a further adjustment of the wavelength setting to obtain the maximum deflection to the left by the indicator needle, thus insuring that the wave length is set at the center of the Cd emission line. By further adjustments of the sensitivity control knob and the slit control, balance the indicator with the transmission dial set between 60 and 100%. This reading will be the reference point for

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the standard curve. From time to time during the course of a set of measurements, the 2.10 g/l Cd solution should be remeasured and the instrument reset to give the reference point reading if necessary.

Measure the emission of the remaining standard solutions by balancing the indicator with the transmission dial. Always balance the dark current before each reading. Construct a graph, plotting average per cent transmission readings (% relative emission) versus Cd concentration for each solution.

To determine Cd concentration in a sample, weigh out 4.9-5.1 g. of sample drillings (weigh to within 0.01 g.). Cover with 45 ml. of 4 M HNO_3 and heat strongly in order to dissolve the metal rapidly. When all of the sample has dissolved, transfer the resulting solution to a 100 ml. volumetric flask, cool, and dilute to volume with distilled water.

Measure the emission of the solution, after adjusting the instrument to give the standard reading for the 2.10% Cd solution. Use the same slit width as was used for the standard curve. Measure the emission of an additional standard solution near the center of the curve. If its emission does not agree with the standard curve, a new standard curve should be prepared. (Remark 1)

Calculations

Obtain the Cd concentration of the unknown solution directly from the standard curve. The Cd concentration of the sample is then as follows:

$$\% \text{ Cd} = \frac{10\ A}{B}$$

A = g/l Cd in solution
B = g. sample taken

Remark

1. If it is desired to analyze a sample containing more than 2-4% cadmium, the lead concentration of the solution obtained upon dissolving the sample must be adjusted to within 2-3 g/l of that of the standard solutions, i.e., 48.5 g/l. This may be conveniently done by adding the necessary amount of the 310 g/l $Pb(NO_3)_2$ solution.

Literature References

Brite, D.W., Hanford Works Secret Notebook, HW-5377-T.

Written by: D. W. Brite
Date: April, 1953

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DETERMINATION OF CERIC ION

Volumetric Method

Principle

Ceric ion is reduced by an excess of arsenious acid with osmium tetroxide present as a catalyst. Osmium tetroxide acts as an electron carrier and does not affect the final titration. The excess arsenious acid is titrated with standardized ceric sulfate, using ferroin as an internal indicator. The endpoint is determined visually.

Other oxidizing agents, if present, will interfere with the method.

$$2H_4Ce(SO_4)_4 + H_3AsO_3 + H_2O \xrightarrow{(OsO_4)} Ce_2(SO_4)_3 + H_3AsO_4 + 5H_2SO_4$$

Solutions

Arsenious acid, 0.1 N.

Ferroin indicator, 0.025 M.

Standardized ceric sulfate, 0.1 N.

Osmium tetroxide, 0.01 M - 1 g. OsO_4 in 2.2 ml. conc. H_2SO_4 and 400 ml. H_2O.

Procedure - Analysis of Ceric Ammonium Sulfate

Accurately weigh 1 g. of sample and dissolve in 1 ml. concentrated sulfuric acid and 10 ml. water. Add one drop of ferroin indicator and four or more drops of osmium tetroxide solution. Add 25 ml. of 0.1 N arsenious acid. Titrate with standardized 0.1 N ceric sulfate until the indicator changes from red to blue. Carry a reagent blank through the procedure, using 25 ml. 0.1 N arsenious acid.

Calculations

$$\% \ (NH_4)_2Ce(NO_3)_6 = \frac{(A - B)\ C \times 0.5483 \times 100}{D}$$

A = ml. of ceric sulfate for blank titration
B = ml. of ceric sulfate for sample titration
C = normality of ceric sulfate
D = grams of sample.

Literature References

1. Smith, G. F., "Cerate Oxidimetry", G. F. Smith Chemical Co., Columbus, Ohio, 41, (1943).

Written by: M. W. Gift
Date: July, 1952

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DETERMINATION OF CHLORIDE

Volumetric Method

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Principle

Sodium chloride reacts with silver nitrate to precipitate silver chloride. The excess silver nitrate is then titrated with potassium thiocyanate, using ferric alum as an indicator. The silver thiocyanate precipitates, and when all the silver ions are removed, ferric thiocyanate forms, as indicated by the formation of a red color. The first tinge of a permanent pink in the solution indicates the endpoint of the reaction.

If the reaction flask stands exposed to light, the silver salts darken and turn gray. This obscures the endpoint and tends to give low values.

$$NaCl + AgNO_3 \xrightarrow{HNO_3} AgCl + NaNO_3$$

$$AgNO_3 + KSCN \longrightarrow AgSCN + KNO_3$$

$$6KSCN + 2(NH_4)Fe(SO_4)_2 \longrightarrow 2Fe(SCN)_3 + 3K_2SO_4 + (NH_4)_2SO_4$$

Solutions

Standardized potassium thiocyanate, 0.1 N.

Ferric alum indicator, saturated. Dissolve 140 g. of ferric ammonium sulfate ($Fe(NH_4)(SO_4)_2 \cdot 12H_2O$) in 400 ml. hot water. Cool and filter into a 500 ml. volumetric flask. Add 40 ml. concentrated nitric acid and dilute to the mark.

Procedure - Analysis of Sodium Chloride (Rock Salt)

Dry several grams of rock salt sample at 105-110°C for several hours, preferably overnight. Weigh 0.20-0.25 g. into a 300 ml. Erlenmeyer flask and dissolve in 20 ml. of distilled water. Add 5 ml. concentrated nitric acid and exactly 50 ml. of 0.1 N silver nitrate solution, mix thoroughly, and allow to stand in a dark cupboard for 30 min. (Remark 1).

Add about 3 ml. of ferric alum indicator and titrate with standardized potassium thiocyanate until the first permanent pink color is reached. Carry a reagent blank through the procedure.

Calculations

$$\% \text{ NaCl} = \frac{(A - B) \times N \text{ of KSCN} \times 5.845}{\text{g. sample}}$$

A = ml. KSCN for blank
B = ml. KSCN for sample.

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Remarks

1. The endpoint may be easier to see if the silver chloride is filtered out at this point. If this is done, the filter paper, flask, and precipitate should be thoroughly washed with several portions of 1:99 nitric acid.

References

1. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., 392 (1937).

Written by: M. C. Lambert
Date: July, 1952

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DETERMINATION OF CHLORIDE

Turbidimetric Method

Principle

Silver ion forms a sufficiently reporducible turbidity with chloride ion to provide a means of estimating spectrophotometrically the chloride ion. The sample must be dissolved in water and freed from interferences, which is the purpose of the specific procedures given below. Among these interferences are lead, palladium, monovalent mercury, monovalent copper, monovalent thallium, iodides, bromides, cyanides, thiocyanates, thiosulfates, and strongly colored solutes. The final solution should contain only a very slight excess of silver nitrate and nitric acid. Excessive amounts of either of these materials promotes dissolution of the silver chloride and causes low results. Chloride free water must be used for all reagents and dilutions.

Solutions

Silver nitrate. Dissolve 17 g. $AgNO_3$ in 1 l. 35% nitric acid (dil.conc. nitric acid 1:1).

Standardized chloride, 0.1 mg. Cl per ml. Dissolve 4.120 g. NaCl in 1 l. water.

Procedure - Analysis of Chromium Nitrate, Cobalt Nitrate, Ceric Ammonium Nitrate, Ferrous Ammonium Sulfate

Dissolve a 5 g. sample in 35-40 ml. water, filter into a 50 ml. volumetric flask, and dilute to the mark with filter washings. Transfer a 25 ml. aliquot of this solution to a second 50 ml. volumetric flask, add 1 ml. of 1:1 nitric acid, and dilute with water to the mark. Carry the other 25 ml. through the general procedure (aliquot = 0.50), using the above acidified dilution as the blank (Remark 1).

Procedure - Analysis of Sodium Nitrate

Dissolve a 1 g. sample in water and dilute to 100 ml. Carry 10 ml. of this solution (aliquot = 0.10) through general procedure.

Procedure - Analysis of Sodium Sulfate (10 H_2O), Sodium Sulfate (Anhydrous)

Carry a 0.5 g. sample through general procedure (aliquot = 1.00).

Procedure - Analysis of Lanthanum Ammonium Nitrate, Oxalic Acid

Carry a 2 g. sample through general procedure (aliquot = 1.00).

Procedure - Analysis of Silver Nitrate

Carry a 5 g. sample through general procedure (aliquot = 1.00).

Procedure - Analysis of Zirconyl Gel

Dissolve a 2 g. sample in the smallest possible quantity of 50% sulfuric acid and continue according to general procedure (aliquot = 1.00).

Procedure - Analysis of Bismuth Subnitrate

Dissolve a 5 g. sample in the smallest possible quantity of conc. nitric acid and carry through general procedure (aliquot = 1.00).

Procedure - Analysis of Sodium Bismuthate

Add 2 g. of sample to 25 ml. of water and boil for 10 min. Filter and wash filter with 10-15 ml. of water. Carry through general procedure on combined filtrate and washings (aliquot = 1.00).

Procedure - Analysis of Calcium, Sodium Hydroxide, Potassium Hydroxide

Dissolve a 1 g. sample (use 10 g. potassium hydroxide) in 50 ml. of water, acidify with 1:1 nitric acid until acid to litmus (Remark 2), transfer to a 100 ml. volumetric flask and dilute to volume. Carry 5 ml. of this solution (aliquot = 0.05) through the general procedure.

Procedure - Analysis of Aluminum Nitrate

Weigh out 5 g. of sample and carry through general procedure (aliquot = 1.00).

Procedure - Analysis of Hydrofluosilicic Acid

Carry 2 g. of 27-30% acid (1.6 ml.) through general procedure (aliquot = 1.00).

Procedure - Analysis of Nitric Acid, 60% and 95%

Carry 2 g. of 60% acid (1.46 ml.) or 2 g. 95% acid (1.35 ml.) through general procedure (aliquot = 1.00).

Procedure - Analysis of Phosphoric Acid, 85%.

Carry 10.0 g. (5.9 ml.) through general procedure (aliquot = 1.00).

Procedure - Analysis of Manganous Nitrate

Carry 1.00 g. (0.65 ml.) through general procedure (aliquot = 1.00).

Procedure - Analysis of Trichlorethylene (Permachlor)

Place 10 g. of sample in a separatory funnel with 20 ml. of water and shake vigorously for 2 min. Allow to settle, then drain off and discard lower organic layer. Carry 10 ml. of the upper aqueous layer through the general procedure (aliquot = 0.50).

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Procedure - General

Dissolve the sample in a small volume of water. If the solution is not clear, it must be filtered, and the filter washed. Transfer the combined filtrate and washings (or aliquot from any of the procedures given above) to a 50 ml. volumetric flask and dilute to 40-45 ml. with water. Add 1 ml. of acid silver nitrate (Solution 1), dilute to the mark, and mix. Transfer the solution to a 19 mm. Coleman cuvette. Insert the PC-4 filter into the spectrophotometer (Coleman Model 11), adjust the wavelength setting to 400 mu, and measure the transmittance of the solution against a distilled water blank. From the calibration curve (Remark 3), determine the grams of chloride present in the aliquot.

Calculations

$$\% \text{ Cl}^- = \frac{\text{g. Cl}^- \text{ (from curve) x 100}}{\text{g. sample x aliquot}}$$

Remarks

1. By this means the same concentration of colored ion is incorporated in the blank as in the sample solution, and all light absorption effects are cancelled except those arising from the precipitated silver chloride. A separate calibration curve (Remark 3) must be prepared for each colored salt.

2. Caution: Considerable heat is evolved in the neutralization of 10 g. potassium hydroxide. About 30 ml. of 35% acid is required, and this must be added slowly to avoid boiling and spitting. All solutions must be allowed to cool to room temperature before diluting to volume.

3. To prepare the standard curve, deliver into separate 50 ml. volumetric flasks 0, 1, 5, 10, 20, and 40 ml. portions of the chloride standard solution (Solution 2), corresponding respectively to 0, .0001, .0005, .0010, .0020, and .0040 g. of Cl^-. Dilute each sample to about 40 ml., add 1 ml. of acid silver nitrate (Solution 1), dilute to volume and mix. Measure the transmittance of each solution on the Coleman Model 11 spectrophotometer according to the general procedure. Plot on single cycle semi-log paper the per cent transmittance of each solution as ordinate against the amount (in grams) of chloride in each solution.

Literature References

1. A.C.S., "Specifications for Analytical Reagents", (1942).

2. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., (1939).

3. Hillebrand and Lundell, "Applied Inorganic Analysis", John Wiley and Sons, Inc. (1929).

Written by: J. E. Meinhard
Date: July, 1952

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DETERMINATION OF COMBINED CHLORIDE AND BROMIDE

Turbidimetric Method

DECLASSIFIED

Principle

Silver chloride and silver bromide are soluble in ammonium hydroxide; silver iodide is insoluble and may be separated from a mixture of the three halides by filtration. Acidification of the filtrate destroys the soluble silver-ammonium complexes and reprecipitates the halides. The combined chloride and bromide may then be estimated turbidimetrically. If free halogen is present in the original sample, it must first be reduced to halide by some agent, such as sulfurous acid. Cyanides, thiosulfates, thiocyanates, and strongly colored ions interfere.

Solutions

Standardized chloride, 0.1 mg. Cl per ml. Dissolve 4.120 g. NaCl in 1 l. water.

Procedure - Analysis of Iodine

Grind 5 g. sample with 25 ml. water, let stand for 30 min. with occasional stirring and filter. To 20 ml. of the filtrate add sulfurous acid until the amber color disappears. Avoid an excess. Carry through general procedure, using 2 ml. of standardized chloride as comparison standard (aliquot = 0.80).

Procedure - Analysis of Hydriodic Acid, 47%

Dilute 1.42 ml. (sample = 1 g.) to 100 ml. Take aliquots of 1 ml. and 5 ml. To the 1 ml. aliquot add 0.4 ml. of standardized chloride. Carry the 5 ml. aliquot through the general procedure, using the 1 ml. aliquot as comparison standard (aliquot = 0.04).

Procedure - General

Dilute the sample aliquot and the comparison standard to 25 ml. Add 1 ml. of ammonium hydroxide (28%) to each solution, then add with stirring 2 ml. of 3.5% silver nitrate. Boil gently 5 min., cool thoroughly, and filter (Remark 1). Wash filter with 5 ml. water. Add 1:1 nitric acid dropwise to the filtrate until cloudiness appears; then, add 10 drops in excess. Visually compare turbidity of sample with that of the aliquot (Remark 2).

Calculations

$$\% \text{ Cl(Br)} = \frac{\text{ml. std. chloride} \times 0.01}{\text{g. sample} \times \text{aliquot}}$$

Remarks

1. Caution: Silver-ammonium complexes have been known to form dangerously explosive mixtures on standing. Therefore, do not interrupt the procedure

after the silver nitrate has been added to the ammonia solution. Also do not allow the solution to boil dry.

2. For more accurate work dilute the solutions to a final volume of 50 ml. and compare their transmittancies on a spectrophotometer. A standard curve may be prepared for this purpose, using the standardized chloride solution.

Literature References

1. A.C.S., "Specifications for Analytical Reagents", (1942).

2. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., (1939).

Written by: J. E. Meinhard
Date: July, 1952

DETERMINATION OF CHLORIDE

(Turbidimetric)

Principle

The method is based on the turbidity formed by the reaction of silver nitrate with chloride ion. Other turbidities and certain colored ions interfere. This can be eliminated by splitting the sample and using half as a blank and half as a sample. Silver nitrate is added only to the sample.

Special Apparatus

Beckman Spectrophotometer, 10 cm cells.

Solution

50% NaOH made from colorific grade Na_2O_2.

Standard chloride solution, 1 mg of Cl-/ml.

Procedure

Standard Curve

Pipet 5 ml of standard chloride solution into 250 volumetric flask. Dilute to volume and mix. (This dilution should be made daily). Pipet 1, 2, 4, 6 ml aliquots into a 100 ml stoppered graduate. Dilute to 85 ml. Add 10 ml 95% ethanol, 3 ml 0.2 N Na_2SO_4 and 1 ml 0.1 N $AgNO_3$. Dilute to 100 ml and mix carefully by inversion. Do not shake. Allow to stand in dark 20 minutes (not more than 30 min.). Read against a reagent blank. Plot micrograms Cl^- vs per cent transmission on one cycle semi-log paper.

Analysis of Sample - Chloride in Material 100-61

Weigh 1 g samples in duplicate. Place in 250 ml beaker (Note 1). Add 10 ml NaOH and heat till in solution (Note 2). Dilute to 25 ml and neutralize Ag adding 20 ml con HNO_3 in 2-3 ml portions. Mix thoroughly after each addition. If turbidity persists, heat gently or add more HNO_3 if necessary. Transfer to glass stoppered graduates and dilute to 85 ml. Add 10 ml ethanol, 3 ml 0.2 M Na_2SO_4. Mix carefully by inverting 6 times and pour half of sample into a second graduate. Add 1 ml Ag NO_3 to one half and dilute to both to 50 ml. Mix carefully by inversion. Allow to stand in dark 20 minutes (not more than 30 min.). Read on Beckman spectrophotometer in 10 cm cells at 450 mu. Use first half as blank.

Calculation

$$\text{ppm } Cl^- = \frac{\text{micrograms } Cl^-}{\text{sample weight}}$$

Note 1. All glassware must be free from Cl^-.

Note 2. Colorific grade Na_2O_2 must be used to prepare NaOH as ordinary NaOH is high in Cl^- content.

Literature Reference

Koyama, Karl, Secret Notebook HW-3641-T, p. 55.

Written by: F. P. Roberts
Revised: July 20, 1954

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Page Co-1-1

DETERMINATION OF COBALT

Electrolytic Method

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Principle

Cobalt may be deposited electrolytically from an ammoniacal solution onto a platinum gauze cathode which may be weighed to determine the quantity of cobalt. The elements silver, copper, arsenic, zinc, and nickel interfere by co-deposition.

Procedure - Analysis of Cobalt Nitrate

Weigh accurately 0.2 g. of sample into a beaker. Dissolve with 10 ml. of water and 2 ml. of concentrated sulfuric acid. Evaporate the solution to white fumes. Cool and add 50 ml. of water. Neutralize the solution with concentrated ammonium hydroxide and add 25 ml. excess of concentrated ammonium hydroxide.

Electrolyze at 1.5 amp. for 1 hr., using a tared cathode. Dilute the solution and continue electrolysis. Check for completeness of deposition by observing the freshly covered electrode section.

When deposition is complete, rinse electrodes while lowering beaker with the current on. Remove the cathode, immerse in distilled water, then in alcohol, and dry in an oven at 100°C for 3 min. Cool and weigh.

Calculations

$$\%\ Co(NO_3)_2 \cdot 6H_2O = \frac{\text{g. of cobalt deposited} \times 493.8}{\text{g. of sample}}$$

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Date: August, 1952

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Code Cr-1

DETERMINATION OF CHROMIUM

Volumetric Method

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Principle

Hexavalent chromium is quantitatively reduced to the trivalent state by bivalent iron in acid solution. The endpoint is determined visually by means of an internal indicator.

Trivalent chromium may be quantitatively oxidized to the hexavalent state with peroxydisulfate with silver ion as a catalyst.

$$2Cr(NO_3)_3 + 3(NH_4)_2S_2O_8 + 8H_2O \xrightarrow{AgNO_3} 2(NH_4)_2CrO_4 + 6H_2SO_4 + 2NH_4NO_3 + 4HNO_3$$

$$2(NH_4)_2CrO_4 + 6FeSO_4 + 8H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2(NH_4)_2SO_4 + 8H_2O + Cr_2(SO_4)_3$$

$$Na_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Na_2SO_4 + 7H_2O + Cr_2(SO_4)_3$$

$$2H_4Ce(SO_4)_4 + 2FeSO_4 \longrightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3 + 4H_2SO_4$$

Oxidizing agents other than a hexavalent chromium, if present during the titration, interfere.

Solutions

Standardized ceric sulfate, 0.1 N.

Ferroin indicator, 0.025 M.

Procedure - Analysis of Chromium Nitrate

Weigh accurately 2 g. of sample into a 100 ml. volumetric flask containing 50 ml. of water. Dissolve the salt; dilute the solution to the mark with water and mix. Pipet a 25 ml. aliquot into an Erlenmeyer flask. Add 50 ml. of water, 5 ml. of concentrated sulfuric acid, and 0.01 g. of silver nitrate for each 0.01 g. of chromium. Heat to boiling and add 0.5 g. of solid ammonium persulfate. Continue boiling until the excess persulfate is decomposed as indicated by a permanent pink color upon the addition of 1 drop of 0.1% methyl orange. Cool to room temperature and continue as described under the general procedure.

Procedure - Analysis of Sodium Dichromate

Weigh accurately 1.8 g. of sample into a 500 ml. volumetric flask and dissolve in 300 ml. of water. Dilute to the mark and mix. Pipet a 10 ml. aliquot into an Erlenmeyer flask containing 100 ml. of water and proceed as described in general procedure.

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Procedure - General

Pipet 10 ml. of 0.1 N ferrous ammonium sulfate into the flask, stir, and allow to stand for 5 min. Add one drop of the 0.025 M ferroin solution and titrate with standardized 0.1 N ceric sulfate to a color change from light rose to pale green.

Run a reagent blank using the same amounts of reagents and replacing the sample with 10 ml. of water.

Calculations

$$\% \ Na_2Cr_2O_7 = \frac{(B - A) \times N \times 0.04367 \times 100}{\text{g. sample in aliquot}}$$

$$\% \ Na_2Cr_2O_7 \cdot 2H_2O = \frac{(B - A) \times N \times 0.04968 \times 100}{\text{g. sample in aliquot}}$$

$$\% \ Cr = \frac{(B - A) \times N \times 0.05201 \times 100}{\text{g. sample in aliquot}}$$

A = ml. of ceric sulfate for sample
B = ml. of ceric sulfate for blank
N = normality of ceric sulfate.

References

1. Willard and Young, Ind. Eng. Chem., Anal. Ed., 7, 57 (1935).

2. Smith, "Cerate Oxidimetry", G. F. Smith Co., 1942, p. 69.

Written by: R. E. Ewing
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DETERMINATION OF CHROMIUM

Diphenylcarbazide - Colorimetric

Principle

Diphenylcarbazide gives a soluble red-violet product with chromium(VI) in acid solution. Minute amounts of chromium can be determined colorimetrically on the basis of this reaction, the extinction coefficient being 31,400 at 540 millimicrons, based on dichromate molarity. Mercury(I and II), iron(III), vanadium(V), and molybdenum(VI) can interfere but not seriously under the conditions of the procedure. (Remark 1)

Solutions

Diphenylcarbazide, 0.25%. Dissolve 0.25 g. s-diphenylcarbazide and 4 g. phthalic anhydride in 100 ml. of 95% ethanol (Remark 2).

Chromium standard solution, 0.001 g/l. Dissolve 0.2828 g. potassium dichromate in water and dilute to 1 liter (0.1 g. Cr/l). Dilute 10 ml. of the above to 1 liter to give 1 microgram chromium per milliliter.

Sulfuric acid (non-reducing), 6 N. Add dilute potassium permanganate to hot 6 N sulfuric acid until a very faint pink color persists.

Procedure - Analysis of Nitric Acid

Weigh accurately 3 g. of sample into a beaker (Remark 3). Add 5 ml. of water and neutralize with 6 M sodium hydroxide, adding a 2 ml. excess. Add 1 ml. of 30% hydrogen peroxide and heat the solution to boiling. Continue boiling to destroy the excess peroxide.

Transfer the solution to a 25 ml. volumetric flask and add 1 ml. of 6 N sulfuric acid and 1 ml. of 0.25% diphenylcarbazide. Dilute to the mark and mix. Prepare a reagent blank using all reagents but omitting the sample. Compare the sample and reagent blank in matched 2 cm. cuvettes in the spectrophotometer at 540 millimicrons and read the percent transmittancy.

Compare the transmittancy against the standard curve prepared by carrying 1, 3, 5, 7, and 10 ml. aliquots of the standard chromium solution through the procedure, omitting the peroxide oxidation given in the first paragraph.

Calculations

$$\% \text{ Cr} = \frac{\text{g. chromium in aliquot}}{\text{g. of sample in aliquot}}$$

$$\text{ppm Cr} = \% \text{ Cr} \times 10^4$$

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Remarks

1. If appreciable vandadium is present, the solution will be brownish or reddish brown. In such cases, wait 10-15 min. before comparing in spectrophotometer.

2. This solution is much more stable than the acetone solution formerly used, but should not be used if over one week old.

3. If 2 ml. portion does not give reading within range of standard curve, adjust accordingly.

4. If glassware has been cleaned in chromic acid bath, be sure to rinse thoroughly.

References

1. Sandell, E. B., "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience, 260264 (1950).

2. Snell and Snell, "Colorimetric Methods of Analysis", Vol. 2, 3rd Ed., D. Van Nostrand, 274 (1949).

Written by: U. L. Upson
Date: July, 1952

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Code Cu-1

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Page Cu-1-1

DETERMINATION OF COPPER

Electrolytic Method

Principle

According to the electrolytic method, copper is deposited electrolytically at low current density on a platinum gauze cathode, which may be weighed to determine the quantity of copper. Electrolysis is carried out in a moderately acid medium; high acidity tends to prevent complete deposition. Small amounts of nitric acid are beneficial in depolarizing the electrode and promoting a firm deposit. Elements low in the electromotive series interfere by co-deposition.

Procedure - Analysis of Bronze

Weigh accurately 1 g. of sample and dissolve in 10 ml. of concentrated nitric acid. After the reaction ceases, evaporate to dryness and heat thoroughly 30-60 min. on an asbestoes mat. Wet the residue with concentrated nitric acid and heat for 10 min. Add 50 ml. of water, boil the solution, and digest on the steam bath for one hour.

Filter the solution and wash the precipitate with hot water. Add 5 ml. of concentrated sulfuric acid to the combined filtrate and washing, and evaporate to dense white fumes. Cool the solution, transfer to a 250 ml. volumetric flask, and dilute to mark.

Transfer a 100 ml. aliquot to a 250 ml. beaker and add 1.5 ml. of concentrated nitric acid. Proceed as described under "General".

Procedure - Analysis of Copper

Weigh accurately 1 g. of sample. Add 10 ml. of concentrated nitric acid, and when the reaction slows, add 5 ml. of concentrated sulfuric acid.

Evaporate to sulfuric fumes, cool, and wash into a 250 ml. volumetric flask. Make to volume.

Transfer a 50 ml. aliquot to a 250 ml. beaker, add 3-5 ml. concentrated sulfuric acid, and 1-1.5 ml. concentrated nitric acid. Dilute to about 100 ml., and proceed as described under "General".

Procedure - General

Electrolyze for 45 min. at 0.8 amp., using a tared cathode. Dilute the solution and continue electrolysis. Check for completeness of deposition by observing the freshly covered electrode section.

When deposition is complete, rinse electrodes while lowering beaker with the current on. Remove cathode, immerse in distilled water, then in acetone, and dry in an oven at 100°C for 3 min. Cool and weigh.

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Calculation

$$\% \text{ Cu} = \frac{\text{g. deposited Cu} \times 100}{\text{g. sample in aliquot}}$$

References

1. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand, 1353, (1939).
2. A.S.T.M., "Chemical Analysis of Metals, 198 (1946).
3. Slomin, Rapid Quantitative Electrolytic Methods of Analysis, 19.

Written by: R. E. Ewing
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DETERMINATION OF COPPER

Colorimetric Method

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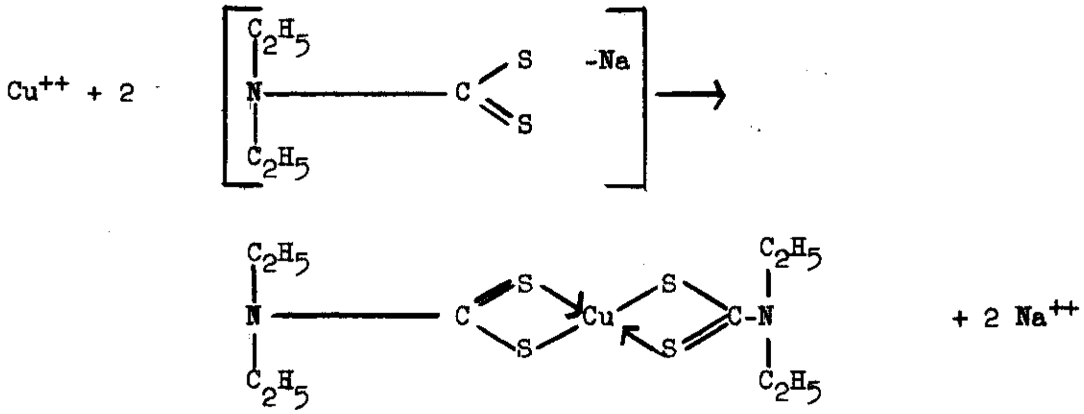
Principle

Dilute solutions of copper salts react with sodium diethyldithiocarbamate at pH's above 9 to form the golden-yellow copper salt of diethyldithiocarbamic acid. The copper salt is soluble in several non-aqueous solvents and is generally extracted before color measurement. The interference of iron is prevented by the use of sodium pyrophosphate.



Solutions

Citrate-pyrophosphate: dissolve 100 g. citric acid and 10 g. sodium pyrophosphate ($Na_4P_2O_7 \cdot 10\ H_2O$) in 400 ml. of water. Add 500 ml. of concentrated ammonium hydroxide and dilute to 1 l.

Sodium diethyldithiocarbamate, 2%, in water.

Standardized copper solution, 0.2 g./l. Dissolve 0.2000 g. of electrolytic copper wire in 20 ml. of 1:1 nitric acid. Boil to remove nitrogen oxides and dilute to 1 l. in a volumetric flask.

Dilute standardized copper solution, 0.01 g./l. Dilute 50 ml. of 0.2 g./l. copper solution to exactly 1 l.

Procedure - Analysis of Al-Si

Dissolve a 5 g. sample in 1:1 hydrochloric acid. When reaction subsides, add sufficient acid to make 200 ml. volume. Boil, filter, and wash with acid. Make filtrate and washings to 500 ml. in a volumetric flask.

Into two separatory funnels add 20 ml. of basic citrate-phosphate solution. Add to one a 2 ml. aliquot and to the other a small quantity of redistilled water to serve as a blank. Mix thoroughly and add 1 ml. of 2% sodium diethyldithiocarbamate solution and mix thoroughly again.

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Add 10 ml. of carbon tetrachloride to each funnel, stopper the funnels, and shake the solutions for 30 sec. Allow the layers to separate and drain off the lower layer through a dry No. 1 Whatman filter paper into a 25 ml. volumetric flask. Repeat the extractions twice, using 5 ml. portions of carbon tetrachloride.

Rinse the filter papers well with small portions of carbon tetrachloride and add these to the volumetric flask. Dilute to the mark with carbon tetrachloride and mix.

Transfer a portion of the sample and blank to matched 10 cm. cuvettes and determine the percent transmittance of the sample against the blank at 450 mu.

Compare the transmittance with a standard curve prepared by carrying 1.0, 2.0, 4.0, and 6.0 ml. of dilute standardized copper solution and 20 ml. of redistilled water through the extraction procedure instead of the sample aliquot.

Calculation

$$\% \text{ Cu} = \frac{\text{g. Cu in aliquot} \times 100}{\text{g. sample in aliquot}}$$

Literature References

1. Report No. C 417.

2. Sandell, "Colorimetric Determination of Traces of Metals, 221-225, (1944).

Written by: R. E. Ewing
Date: July, 1952.

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DETERMINATION OF COPPER

Colorimetric Method

Principle

Copper reacts with ferrocyanide to form a reddish colored compound in dilute acid solutions. The copper must be separated from colored solutions, which mask the copper ferrocyanide color, and must be separated from the interfering element iron. The separation is accomplished by the precipitation of copper as the sulfide from acid solution.

Solutions

Standard copper solution, 0.1 mg./ml. Dissolve exactly 0.1 g. of electrolytic copper wire in 20 ml. of 1:1 nitric acid. Boil to remove nitrogen oxides and dilute to 1 liter in a volumetric flask.

Procedure - Analysis of Cobalt Nitrate

Weigh accurately 2 g. of sample into a beaker and dissolve with 100 ml. of water. Add 2 ml. of concentrated hydrochloric acid and 2 ml. of 1% mercuric chloride. Saturate the solution with hydrogen sulfide. Filter through a small filter and wash with hydrogen sulfide water until filtrate is colorless. Ignite filter and precipitate at 600°C for 1 hr. in a porcelain crucible.

Dissolve the residue in 0.5 ml. of concentrated nitric acid and a few drops of water. Add 5 ml. of water and filter into a Nessler tube. Wash filter several times with water. Add 1 g. of ammonium acetate and 5 drops of freshly prepared 10% potassium ferrocyanide. Dilute to the mark with water.

The color of the sample should not exceed that of a standard prepared by adding the same amounts of all reagents to a Nessler tube containing 1 ml. of the standard copper solution.

References

(1) Furman, N.H., "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand, Inc., New York (1939).

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DETERMINATION OF AMMONIUM FLUOSILICATE

Volumetric Method

Principle

In acid solution, ammonium fluosilicate reacts with a potassium salt to form potassium fluosilicate, K_2SiF_6, which is insoluble in alcoholic medium. Total fluorine present in this precipitate can be estimated by titration with a standard base and calculated as ammonium fluosilicate.

Fluorine present as fluorides and bifluorides does not interfere unless combined with silica.

$$(NH_4)_2SiF_6 + 2KCl \longrightarrow K_2SiF_6 + 2NH_4Cl$$

$$K_2SiF_6 + 4NaOH \longrightarrow 2KF + 4NaF + Si(OH)_4$$

Solutions

Standardized sodium hydroxide, 0.1 N.

Potassium chloride, alcoholic. Weigh 37.5 g. of potassium chloride and dissolve in 250 ml. of freshly boiled distilled water. Add 250 ml. of ethanol and mix well. Transfer into a 500 ml. glass stoppered bottle for storage.

Procedure - Analysis of Ammonium Fluosilicate

Weigh accurately 0.15 g. of sample into a beaker. Dissolve in 1 ml. of conc. hydrochloric acid plus 1 ml. of distilled water, and add 4 g. of potassium chloride. Add 25 ml. of 95% ethyl alcohol, stir, and let stand one hour.

Prepare a Gooch filter. Filter and wash with alcoholic potassium chloride solution until all excess acid is removed. Transfer the filter containing the residue to the original beaker and add 50 ml. of boiling distilled water.

Heat while titrating with standardized 0.1 N sodium hydroxide, using 2 drops of 1.0% alcoholic solution of phenolphthalein as indicator. Finish titration in a boiling solution to a permanent faint pink color.

Calculations

$$\% \ (NH_4)_2SiF_6 = \frac{\text{ml. NaOH} \times \text{N. NaOH} \times 4.454}{\text{g. sample}}$$

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DETERMINATION OF R_2O_3

Gravimetric Method

Principle

The sample is converted to a soluble form and the insoluble hydroxides of the R metal ions are ignited to R_2O_3.

Anions, such as phosphate, arsenate, vanadate, and silicate, form insoluble compounds and must be absent. Organic materials, as tartaric acid or sugar, form soluble complexes with iron and aluminum, and must therefore be removed. Oxidizing agents, such as bromine, may oxidize divalent manganese and cause its precipitation. In the absence of phosphate or carbonate, the alkali and alkaline earth metals present no difficulties when sufficient ammonium salt is present.

$$R^{+++} + 3NH_4OH \longrightarrow R(OH)_3 + 3NH_4^+$$

$$2R(OH)_3 \xrightarrow{\Delta} R_2O_3 + 3H_2O$$

Procedure - Analysis of Magnesium Oxide

Weigh accurately a 1 g. sample into a platinum crucible, add 5 g. sodium carbonate, mix, and cover. Heat cautiously until the mixture becomes a clear and homogeneous melt.

After the molten mass has solidified on the sides of the crucible, immerse the crucible and cover in a beaker of water and heat to effect solution of the contents. After the crucible has been rinsed and removed, add 20 ml. of perchloric acid, and boil the solution for 15 min. after copious fumes of the perchloric acid evolve. Do not permit the contents of the beaker to become solid or the silica separation will be incomplete.

Cool the contents of the beaker, dilute 1:5 with distilled water, heat to boiling, and quantitatively remove the silica by filtration through Whatman No. 42 filter paper. Wash with 1:99 hydrochloric acid and then with water until washings are acid free. Dilute the filtrate and washings to 250 ml. Take a 50 ml. aliquot and add 15 ml. of concentrated hydrochloric acid. Continue according to the general procedure.

Procedure - Analysis of Manganous Nitrate

Weigh accurately 20 g. of sample, transfer to a beaker, and add 50 ml. of water and 15 ml. of concentrated hydrochloric acid. Proceed as described in the general procedure.

Procedure - Analysis of Oxalic Acid

Weigh accurately 20 g. of sample and transfer to a platinum dish. Heat slowly and carefully with a Bunsen flame until the acid melts; ignite the fumes given

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off in order to obviate the danger of explosive air-fume mixtures. After the residue has been ignited, add 5 g. of potassium acid sulfate or potassium pyrosulfate, and fuse until the melt is clear. Extract the melt with 100 ml. of distilled water to which has been added 15 ml. of concentrated hydrochloric acid and continue as indicated in the general procedure.

Procedure - General

Add 1 ml. of concentrated nitric acid to the solution and boil for 5 min. Filter through a No. 40 Whatman paper and wash with water.

Add a few drops of methyl red (0.2% alcoholic solution) and heat just to boiling. Carefully add dilute ammonium hydroxide drop by drop until the color of the solution changes to a distinct yellow. Boil gently for 1-2 min. and filter immediately through a No. 41 Whatman paper or OK Swedish paper. Wash the precipitate thoroughly with hot, 2% ammonium chloride and then suck dry (Remark 1).

Place the paper and precipitate in a tared platinum crucible and cautiously smoke off the paper. Ignite the crucible in a muffle at 900°C and accurately weigh the residue.

Calculations

$$\% \ R_2O_3 = \frac{\text{g. residue} \times 100}{\text{g. sample in aliquot}}$$

Remarks

1. If the nature or amounts of other elements present call for it, dissolve the precipitate in 25 ml. of 1:4 hydrochloric acid and reprecipitate as before.

References

1. Treadwell and Hall, "Analytical Chemistry", John Wiley and Sons, Inc., Ed. 9, Vol. II, 148-171 (1937).

2. Griffin, Technical Methods of Analysis", McGraw-Hill Book Co., Inc., 148 (1927).

3. Kolthoff and Sandell, "Testbook of Inorganic Quantitative Analysis", MacMillan Co., 294-307 (1936).

4. Hillebrand and Lundell, "Applied Inorganic Analysis", John Wiley and Sons, Inc., 341, 397 (1929).

Written by: T. K. Bierlein
Date: July, 1952

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DETERMINATION OF IRON

Volumetric Oxidation Method

Principle

Ceric ion quantitatively oxidizes ferrous ion to ferric and thus may be used as a titrating agent for the determination of ferrous iron. The titration is carried out in acid medium in order to hold the salts in solution. Ferriron indicator, ferrous o-phenanthroline, serves as the indicator in that the first excess of ceric ion destroys the red complex. Other reductants interfere.

Solutions

Ferroin indicator, 0.025 M.

Standardized ceric sulfate solution, 0.1 N.

Procedure - Analysis of Ferric Sulfate (Ferri Floc)

Weigh accurately 5 g. of sample and dissolve in 100 ml. of boiling water. Filter, wash into a 500 ml. volumetric flask, and dilute to volume. Transfer two 50 ml. aliquots to separate Erlenmeyer flasks. Add to each 20 ml. of approx. 6 N sulfuric acid. To one aliquot add 2 drops of ferroin indicator and titrate with standardized ceric sulfate solution to the disappearance of the red color. Calculate the amount of ferrous iron in the ferric sulfate.

To the other aliquot add 100 ml. of water and reduce the iron in a Jones Reductor. Rinse the reductor with 100 ml. of 1 N sulfuric acid, followed by 100 ml. of water leaving the reductor filled with water. Add 2 drops of ferroin indicator and titrate the iron with standardized ceric sulfate to the disappearance of the red color.

Procedure - Analysis of Ferrous Ammonium Sulfate

Weigh accurately 5 g. of sample and dissolve in a solution of 150 ml. of water and 20 ml. of sulfuric acid in a 500 ml. volumetric flask. Transfer a 50 ml. aliquot to an Erlenmeyer flask and add 2 drops of ferroin indicator. Titrate with standardized ceric sulfate to the disappearance of the red color.

Titrate a reagent and water blank, and obtain a correction for any iron present in the water.

Calculations

$$\% \text{ Iron Compound} = \frac{(A - B) \times N \times F}{\text{g. of sample}}$$

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A = ml. of ceric sulfate for sample
B = ml. of ceric sulfate for blank
F = 199.9 for ferric sulfate ($Fe_2(SO_4)_3$)
F = 151.8 for ferrous sulfate ($FeSO_4$)
F = 392.1 for ferrous ammonium sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$)

Literature References

1. Hillebrand and Lundell, "Applied Inorganic Analysis", John Wiley and Sons, Inc., 580 (1929).

2. Furman, "Scott's Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand Co., Inc., 474-476 (1939).

Written by: C. A. Goodall
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IRON DETERMINATION

Colorimetric Method
Range 20 to 120 micrograms

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Principle

O-phenanthroline reacts with ferrous iron in slightly acid solution (pH 3-6) to form a red-colored complex. In order to determine total iron, it is necessary to reduce any ferric iron present by means of hydroxylamine hydrochloride.

Substances precipitated by ammonium hydroxide (group III Al, V, etc.) interfere by precipitating at the pH used. The addition of 1 ml. of 10% ammonium or sodium citrate prevents such interference. The addition should be made just before neutralizing. No other interference has been encountered.

Solutions

Ortho-phenanthroline solution, 0.1%. Dissolve 0.5 g. ortho-phenanthroline in 50 ml. of distilled water in a 500 ml. volumetric flask and dilute to the mark with distilled water.

Standard ferrous sulfate solution, 1 ml. = 10 micrograms of iron. Carefully add 50 ml. concentrated sulfuric acid to 250 ml. of distilled water in a 500 ml. volumetric flask. Dissolve 0.0351 g. of ferrous ammonium sulfate in this solution and dilute to volume with distilled water.

Procedure - Analysis of Aluminum and Al-Si

Weigh accurately a 5.00 g. sample and dissolve with 200 ml. of 1:1 hydrochloric acid. Boil the solution for at least 5 min., or until solution is clear. Filter into a 500 ml. volumetric flask and wash with hot water. Dilute the filtrate to volume. Using a 2 ml. aliquot, proceed as described in the general procedure.

Procedure - Analysis of Aluminum Nitrate (ANN)

Weigh accurately a 10.0 g. sample of aluminum nitrate solution into a beaker and add 25 ml. of concentrated sulfuric acid and 5 ml. of water. Add formic acid and heat if necessary to remove the nitrate; continue the formic acid addition until no brown fumes are expelled. Heat the solution until white fumes are observed, cool, and add 100 ml. water. Heat to dissolve crystals and filter into a 250 ml. volumetric flask. Dilute to volume with water. Using a 1 ml. aliquot, proceed as described in the general procedure.

Procedure - Analysis of Bismuth

Weigh accurately 5.00 g. of sample into a beaker and dissolve with 60 ml. concentrated nitric acid. Boil to complete dissolution. Cool and add 100 ml. of 10% nitric acid. Filter through a sintered glass crucible and wash with

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10% nitric acid. Heat to boiling and add 5 ml. 10% barium chloride. Allow to stand at least two hrs., then filter into a 500 ml. volumetric flask. Wash with 10% nitric acid and dilute to volume with 10% nitric acid. Using a 20 ml. aliquot, proceed as described in the general procedure.

Procedure - Analysis of Chromium Nitrate Salt

Weigh accurately 2.50 g. sample and dissolve with 50 ml. of water, 5 ml. of 50% sodium hydroxide, and 5 ml. of 30% hydrogen peroxide. Boil to expel the excess peroxide. Acidify with HCl, neutralize with NH_4OH, and boil to expel excess ammonia. Filter and wash the precipitate with cold water, discarding filtrate. Dissolve the precipitate with 10 ml. of hot 1:1 HCl. Transfer the solution through a filter into a 100 ml. volumetric flask and wash filter with hot water. Using a 10 ml. aliquot, proceed as described in the general procedure.

Procedure - Analysis of Cobalt Nitrate

Weigh accurately 10 g. of sample into a beaker. Dissolve with 2 ml. of concentrated hydrochloric acid, 40 ml. of water, and 5 drops of concentrated nitric acid. Heat to boiling and add an excess of 3 M ammonium hydroxide, dissolving the precipitate which first forms. Filter the precipitate from the solution and wash with 1 M ammonium hydroxide until washings are colorless. Dissolve the precipitate with 10 ml. of hot 10% hydrochloric acid into a 100 ml. volumetric flask. Wash the filter several times with water. Dilute the solution and washings to the mark. Using a 10 ml. aliquot, proceed as described under "General".

Procedure - Analysis of Fluosilicic Acid

Weigh accurately 10 g. of sample into a platinum crucible. Add 10 ml. of concentrated hydrofluoric acid, evaporate to dryness, and ignite at 400°C Add 5 ml. of concentrated hydrochloric acid and evaporate to dryness. Dissolve the residue with 8 ml. of concentrated hydrochloric acid, transfer the solution to a 100 ml. volumetric flask and dilute to the mark. Using a 10 ml. aliquot, proceed as described under "General".

Procedure - Analysis of Hydrogen Peroxide

Weigh accurately 100 ml. of sample into a platinum dish. After evaporating to dryness, rinse down the sides with 2 ml. of hydrochloric acid and 5 ml. water. Re-evaporate to 1-2 ml. volume and transfer to the 50 ml. volumetric flask. Using the entire sample, proceed as described in the general procedure.

Procedure - Analysis of Nitric Acid

Weigh into a tared 250 ml. beaker a 50 ml. sample of nitric acid. Evaporate to dryness and dissolve the residue in 2 ml. of concentrated hydrochloric acid. Using the entire sample, proceed as described in the general procedure.

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Procedure - Analysis of Oxalic Acid

Weigh accurately a 5.00 g. sample and ignite in a porcelain crucible. Dissolve the cool residue with 2 ml. of concentrated hydrochloric acid and 5 drops of concentrated nitric acid. Transfer to a 100 ml. volumetric flask and dilute to volume with water. Using a 10 ml. aliquot, proceed as described in the general procedure.

Procedure - Analysis of Phosphoric Acid

Weigh accurately a 1 ml. sample. Using the entire sample proceed as described in the general procedure.

Procedure - Analysis of Potassium Hydroxide

Weigh accurately a 20.0 g. sample into a 100 ml. volumetric flask. Dissolve with 30-40 ml. of distilled water. Neutralize with concentrated hydrochloric acid, adding a slight excess. Cool and dilute to volume. Using a 10 ml. aliquot, proceed as described in the general procedure.

Procedure - Analysis of Sulfuric Acid

Weigh accurately a 1 ml. sample into a 100 ml. volumetric flask. Dilute to volume and mix. Using a 10 ml. aliquot, proceed as described in the general procedure.

Procedure - General

Deliver the specified aliquot into a 50 ml. volumetric flask. Add 1 ml. of 10% hydroxylamine hydrochloride and mix solution. Add 1 ml. of ortho-phenanthroline and 5 ml. of 10% ammonium citrate. Adjust the pH of the solution 3-6 with 1 M hydrochloric acid or 1 M ammonium hydroxide as required. Dilute to mark with water and mix solution. Compare in spectrophotometer at 515 mu against sample blank prepared in the same manner and containing all reagents except ortho-phenanthroline, using 2 cm. cuvettes.

Compare the transmittancy obtained against the transmittancy obtained by carrying 1, 3, 5, and 7 ml. of the standard iron solution through the same procedure.

Calculations

$$\% \text{ Fe} = \frac{\text{g. Fe in aliquot} \times 100}{\text{g. sample in aliquot}}$$

$$\text{ppm Fe} = \% \text{ Fe} \times 10^4$$

References

1. Smith, G. F., "Phenanthroline and Substituted Phenanthroline Indicators," The G. Fredrich Smith Chemical Co., Columbus, O., 103 pp. (1944).

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HYDROGEN ION, ACID ASSAY

Volumetric Method

Principle

The acid assay can most easily be accomplished by determining the amount of standardized base needed to neutralize the acid present in the sample taken for analysis. The equivalence point is determined by noting the change in color of an acid-base indicator. The indicator must be selected such that the color change occurs at the equivalence point.

The interferences in this method are the presence of acids other than the acid being assayed.

Solutions

Standardized sodium hydroxide solution, 0.1 N.

Procedure - Analysis of Fluosilicic Acid

Weigh accurately 0.25-0.3 g. of sample into an Erlenmeyer flask containing 25 ml. of water. Titrate to a pink color with standardized sodium hydroxide. Heat to 80°C and complete the titration to the endpoint, using 1 drop of 1% phenolphthalein as the indicator.

Procedure - Analysis of Hydriodic Acid

Weigh accurately 0.25-0.35 g. of sample into an iodine flask containing 25 ml. of water. Add just enough 0.1 N sodium thiosulfate to remove the iodine color. Titrate the sample with 0.1 N sodium hydroxide to the endpoint, using 2 drops of 1% phenolphthalein as the indicator.

Procedure - Analysis of Nitric Acid

Weigh accurately 0.2-0.25 g. of sample into an Erlenmeyer flask containing 25 ml. of distilled water. Titrate the sample with 0.1 N sodium hydroxide to the endpoint, using 1 drop of 0.1% alcoholic solution of methyl red as the indicator.

Procedure - Analysis of Phosphoric Acid

Dissolve 5 g. of sodium chloride in 25 ml. of water. Add 3 drops of 1% thymolphthalein indicator and adjust solution to neutrality. Weigh accurately 0.15-0.2 g. of sample into the neutral solution. Titrate the sample with 0.1 N sodium hydroxide to the endpoint.

Procedure - Analysis of Sulfuric Acid

Weigh accurately 0.1-0.14 g. of sample into an Erlenmeyer flask containing 25 ml. of water. Titrate the sample with standardized sodium hydroxide to the endpoint, using 1 drop of 0.1% alcoholic solution of methyl red as the indicator.

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Calculations

$$\% \text{ of the Acid} = \frac{(\text{ml. of NaOH})(\text{Normality of NaOH})(F)(100)}{\text{g. of sample}}$$

$F = 0.07204$ for fluosilicic acid
$F = 0.1279$ for hydriodic acid
$F = 0.06302$ for nitric acid
$F = 0.04902$ for phosphoric acid
$F = 0.04904$ for sulfuric acid.

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand Co., 2229 (1939).

2. Treadwell and Hall, "Analytical Chemistry", 9th Ed., John Wiley and Son, 507 (1937).

Written by: R. E. Ewing
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DETERMINATION OF ACIDITY

Volumetric Method

Principle

The sample is titrated with sodium hydroxide to the phenolphthalein endpoint to determine the acid content.

Solutions

Phenolphthalein, 1%. Dissolve 5 g. phenolphthalein, $C_{20}H_{14}O_4$, commercial dye, in 250 ml. 95% ethyl alcohol in a 500 ml. volumetric flask. Dilute to the mark with the alcohol. Mix well and transfer to a glass stoppered bottle.

Standardized sodium hydroxide, 0.1 N.

Procedure - Analysis of Hexone, Methanol, Tributylphosphate

Pipet a 50 ml. sample into 50 ml. of distilled water in an Erlenmeyer flask. Add 3 drops of phenolphthalein and titrate with 0.1 N sodium hydroxide to a faint pink endpoint which persists for 30 sec. Shake the flask vigorously after each addition of sodium hydroxide.

For a blank, titrate 50 ml. of the distilled water, to which 3 drops of phenolphthalein have been added, with 0.1 N sodium hydroxide.

Calculations

$$\text{Acidity, as normality} = \frac{\text{ml. of std. NaOH (sample - blank)} \times \underline{\text{N}} \text{ of NaOH}}{50}$$

$$\text{Acidity, as acetic acid, wt. \%} = \frac{\text{ml. of std. NaOH (sample - blank)} \times \underline{\text{N}} \text{ of NaOH} \times 6.003}{50 \times \text{sp.gr. of sample}}$$

$$\text{Acidity, as acetic acid, vol. \%} = \frac{\text{ml. of std. NaOH(sample - blank)} \times \underline{\text{N}} \text{ of NaOH} \times 5.72}{50}$$

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DETERMINATION OF FREE ACID

Volumetric Method

Principle

Free acid is determined by direct titration after the hydrolyzable materials are complexed with potassium oxalate to prevent hydrolysis.

$$Al^{+++} + 3C_2O_4^{=} + Al(C_2O_4)_3^{\equiv}$$

$$Al^{+++} + H_2O \neq Al(OH)_3 + 3H^+$$

Solutions

Standardized sodium hydroxide, 0.1 N.

Standardized nitric acid, 0.1 N.

Procedure - Analysis of Aluminum Nitrate

Weigh accurately 10 g. of sample into a beaker. Add 10 ml. distilled water to dissolve the sample.

Adjust a pH meter, checking the meter and electrodes with standard buffer mixtures. Immerse the electrodes in the beaker containing the sample, so that the electrodes are not touching the beaker bottom or walls.

Add potassium oxalate crystals in small portions until further addition causes little change in the pH. (The pH should be about 4.7) If the pH rises to 7, spike the samples with a known amount of standard nitric acid and add oxalate crystals again.

Titrate the solution with 0.1 N sodium hydroxide, making the additions in small increments. Measure the pH after the addition of each increment and record the volume of reagent and pH. Continue the titration until a large change in pH, which indicates the endpoint, is passed.

Calculations

ml. NaOH at endpoint = total ml. NaOH added from all increments preceding A +

$$\frac{A - B}{2A - C} \times D$$

A = maximum change in pH in one increment
B = change in pH for increment preceding A
C = " " " " " following A
D = increment used in titration

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$$\text{Free acid, as } HNO_3\% = \frac{\text{ml. NaOH* x } \underline{N} \text{ NaOH x } 6.302}{\text{wt. sample}}$$

*An appropriate correction to the volume of NaOH used must be made if an acid spike is added.

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DETERMINATION OF METHYL ORANGE ALKALINITY

Volumetric Method

Principle

The sample is titrated with standard hydrochloric acid to the methyl orange endpoint which is at a pH of about 3.7. At this pH the strong alkalis, as well as the weak ones such as carbonate, will be completely neutralized so that this is a measure of the total alkalinity of the solution.

Solutions

Standard hydrochloric acid, 0.1 N.

Procedure - Analysis of Sodium Bicarbonate

Weigh accurately 2 g. of sample into a 250 ml. volumetric flask. Dissolve with 100 ml. of water, dilute to the mark, and mix. Titrate a 25 ml. aliquot with standard 0.1 N hydrochloric acid, using 1 drop of 0.1% methyl orange as indicator, to a faint pink color. Calculate the result as % $NaHCO_3$.

Procedure - Analysis of Sodium Carbonate

Weigh accurately 7 g. of sample and place in a 500 ml. volumetric flask containing 100 ml. of water. Shake and mix before and after dilution to volume with water. Transfer a 10 ml. aliquot to an Erlenmeyer flask, add a volume of standardized hydrochloric acid solution calculated to be about 90% of that required for complete neutralization, place a short-stemmed funnel into the neck of the flask, and boil gently to expel carbon dioxide. Cool to room temperature, wash down funnel and flask, add a drop of 0.1% methyl orange, and continue the titration to a faint pink color. Calculate the result as % Na_2O.

Procedure - Analysis of Sodium Hydroxide

Weigh accurately 0.4 g. of sample into a 100 ml. volumetric flask and dissolve with 50 ml. of water. Cool, dilute to mark, and mix. Pipet a 20 ml. aliquot into an Erlenmeyer flask containing 100 ml. of water. Add 1 drop of 0.1% methyl orange and titrate with standard 0.1 N hydrochloric acid to a faint pink color. Calculate the result as % Na_2O.

Procedure - Analysis of Sodium Silicate

Weigh accurately 10 g. of sample into a 250 ml. volumetric flask. Dilute to the mark with water and mix. Titrate a 25 ml. aliquot with standard 0.1 N hydrochloric acid, using 1 drop of 0.1% methyl orange as indicator, to a faint pink color. Calculate the result as % Na_2O.

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Calculations

$$\% \; NaHCO_3 = \frac{A \times B \times 0.0840 \times 100}{\text{g. sample in aliquot}}$$

$$\% \; Na_2O = \frac{A \times B \times 0.0310 \times 100}{\text{g. sample in aliquot}}$$

A = ml. of hydrochloric acid
B = normality of hydrochloric acid.

References

1. American Chemical Society, "Specifications for Analytical Reagents", A.C.S., 104, (1941).

2. Furman, "Scott's Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand Co., 2261 (1939).

3. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., 387 (1939).

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DETERMINATION OF ALKALINITY

Volumetric Method

Principle

The sample is titrated with acid to the methyl orange endpoint to determine the alkali content.

Solutions

Standardized hydrochloric acid, 0.1 N.

Methyl orange, 0.1%, in water.

Procedure - Analysis of Trichloroethylene (Permachlor)

Determine the specific gravity of the trichloroethylene with a hydrometer. Pipet a 25 ml. sample into 100 ml. water in an Erlenmeyer flask. Add 3 drops of methyl orange indicator. Titrate the solution with 0.1 N hydrochloric acid, adding successive portions until the solution shows a permanent faint orange color.

Calculations

$$\text{Alkalinity, as NaOH, wt. \%} = \frac{\text{ml of HCl} \times \text{N HCl} \times 4.00}{25 \times \text{sp.gr. of trichloroethylene}}$$

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DETERMINATION OF ALKALINITY

Volumetric Method

Principle

The alkalinity due to potassium hydroxide alone is obtained by first precipitating the carbonates with barium chloride, then titrating to a phenolpthalein endpoint.

$$K_2CO_3 + BaCl_2 \longrightarrow BaCO_3 + 2KCl$$

$$KOH + HCl \longrightarrow KCl + H_2O$$

The determination of total alkalinity is obtained by continuing the titration to a methyl orange endpoint.

$$BaCO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + CO_2$$

The alkalinity due to carbonates is calculated as the difference between the total alkalinity and that due to potassium hydroxide.

Solutions

Standardized hydrochloric acid, 1 N.

Methyl orange, 0.14. Dissolve 250 mg. methyl orange in 250 ml. water.

Phenolphthalein, 1%. Dissolve 5 g. phenolphthalein in 500 ml. of ethyl alcohol.

Procedure - Analysis of Potassium Hydroxide

Weigh accurately and rapidly 20 g. of potassium hydroxide, dissolve (Remark 1), cool, and dilute to exactly 500 ml. Dilute 50 ml. of this well mixed solution to 200 ml., using distilled water, and add 5 ml. of 10% barium chloride solution. Shake and allow to stand for 5 min.

Add one drop of phenolphthalein and titrate to a faint pink, using the standard hydrochloric acid.

Procedure - Analysis of Potassium Hydroxide - Total Alkalinity

After reaching the phenolpthalein endpoint, add one drop of methyl orange and continue the titration with standard 1 N hydrochloric acid to a permanent red color.

Procedure - Analysis of Potassium Hydroxide - Carbonates

The carbonate present is determined by calculation.

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Calculations

$$\% K_2O = \frac{\text{ml. hydrochloric} \times \underline{N} \text{ hydrochloric} \times 0.04710 \times 100}{\text{g. of sample in aliquot}}$$

$$\% K_2CO_3 = \frac{(A-B) \times 0.0691 \times 100}{\text{g. of sample in aliquot}}$$

A = ml. HCl x $\underline{N}$ HCl required to reach methyl orange endpoint
B = ml. HCl x $\underline{N}$ HCl required to reach phenolpthalein endpoint.

Remarks

1. Throughout the procedure dilutions should be made with freshly boiled, distilled water to prevent addition of carbonates from this source.

Literature References

1. American Chemical Soceity, "Reagent Chemicals", 270 (1941).

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DETERMINATION OF NEUTRALITY

Qualitative Method

Principle

An indicator, phenolphthalein, is used to check the sample for neutrality. This indicator is colored pink in alkaline and is colorless in neutral and acid solutions. If the indicator remains colorless when added to a solution of the sample, a further test is necessary to insure that the sample is not acid. This further test consists of the addition of a small amount of base which, when added to a neutral solution, will make it sufficiently alkaline to color phenolphthalein.

Solutions

Phenolphthalein, 1%. Dissolve 5 g. phenolphthalein, $C_{20}H_{14}O_4$, commercial dye, in 250 ml. 95% ethyl alcohol in a 500 ml. volumetric flask. Dilute to the mark with the alcohol. Mix well and transfer to a glass stoppered bottle.

Procedure - Analysis of Potassium Chloride; Sodium Chloride

Weigh to the nearest 0.1 g. a 5.0 g. sample of the material to be tested on a watch glass. Transfer the sample to a 100 ml. beaker and add 50 ml. distilled water to dissolve the sample. Add 3 drops of phenolphthalein solution. Stir. No color should be produced. If no color develops, add 1 drop of 0.1 N sodium hydroxide solution. Stir. A pink color should be produced. If both conditions are satisfied, the sample is neutral.

References

1. Reagent Chemicals, American Chemical Society Specifications, 1950, p. 258, 324.

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DETERMINATION OF IODINE

Colorimetric Method

Principle

Iodide and iodine are oxidized to iodate by hot bromine water in dilute acid solution. Iodine is liberated by potassium iodide after the bromine is expelled thus giving six times as much iodine as was originally present. The color developed with starch indicator is measured with the Beckman Quartz Spectrophotometer.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Solutions

Potassium iodide	.001 mg I/ml
Starch indicator	
Sulfuric acid	2N
Bromine water	Saturated
Salicylic acid	1.0%
Potassium iodide	5 %

Procedure - Sodium Nitrate

Weigh accurately 10.0 gram sample. Dissolve in 30 ml. water and filter into 100 ml. volumetric flask. Dilute to volume and mix. Pipet 5 ml. into a 50 ml Erlenmeyer flask. Add 2 drops 2N sulfuric acid and 5 drops of saturated bromine water. Heat to boiling until yellow color disappears. Add 2 drops 1 percent salicylic acid while hot. Cool to room temperature, add 3 drops starch solution and 3 drops 5 percent potassium iodide.

Transfer to 10 ml. volumetric flask and dilute to volume.

Transfer a portion of the sample into an absorption cell having a path length of 1 cm. Measure the optical density against a reference cell containing all reagents.

Determine the mg. of iodine from a standard curve prepared by running 0, 1, 2, 3, 4, 5, 6, 7, and 8 ml. of the 0.001 mg/ml iodide standard through the above procedure.

Calculations

$$\text{Percent Iodine} = \frac{\text{mg. Iodine}}{\text{sample wt.} \times \text{aliquot} \times 10}$$

Literature Reference

R. G. Turner, J. Am. Chem. Soc. 52, 2768-73 (1930)

Written By: F. P. Roberts
Date: May, 1956

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DETERMINATION OF LANTHANUM

Gravimetric Method

Principle

The rare earth elements may be separated from other substances by precipitation of the oxalates from distinctly acidic solutions. Upon ignition, the oxalate is decomposed quantitatively to oxide. In the determination of lanthanum, other rare earths, scandium, and thorium will interfere.

Procedure - Analysis of Lanthanum Ammonium Nitrate

Weigh accurately 0.5 g. sample into 200 ml. of water containing 1 ml. of nitric acid. Heat to boiling and add dropwise 25 ml. of 10% oxalic acid solution. Digest for two hours at elevated temperature, then filter and wash with hot water. Ignite the precipitate at 900-950°C to constant weight.

Calculations

$$\% \text{ La} = \frac{\text{g. residue} \times 85.27}{\text{g. sample}}$$

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand Co., 5th Ed., 248 (1939).

2. Lundell and Hoffman, "Outlines of Methods of Chemical Analysis", John Wiley and Son, 87 (1938).

3. Hillebrand and Lundell, "Applied Inorganic Analysis", John Wiley and Son, 433 (1939).

Written by: L. F. Kendall
Date: July, 1952

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DETERMINATION OF LITHIUM

Principle

The intensity of light emission when lithium is heated in an oxyhydrogen flame is measured by a Beckman Flame Photometer. No interference by aluminum is encountered.

Special Apparatus

Beckman spectrophotometer with flame attachment.

Solutions and Reagents

Lithium chloride standard, 1.000 g/l Li.

Procedure

Standard Curve

Pipet 10, 7, 5, 3, 1 ml aliquots of lithium standard into 1000 ml volumetric flasks. Dilute to volume and read on the flamephotometer at 687 mu; 3 psi hydrogen and 20 psi oxygen (remark 1). Care must be exercised to keep gas pressures constant. Plot micrograms of Li vs per cent transmission.

Samples - Determination of Lithium (Material 100-61)

Weigh 0.1 ± .01 g of drillings into 250 ml beakers (weighing should be done as soon after drilling as possible). Dissolve in 10 ml conc. HCl. Transfer to 500 ml volumetric flasks and dilute to volume.

Read as in standards:

$$\% \text{ Li} = \frac{\text{micrograms Li}}{\text{sample wt x 20}}$$

Remark 1. Oxygen must be turned on first and hydrogen turned off first when lighting and extinguishing the flame.

References

Koyama, K. Secret Notebook HW-3641-T.

Written by: F. P. Roberts
Revised: July 20, 1954

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DETERMINATION OF MANGANESE

Volumetric Method

Principle

The permanganate ion is quantitatively reduced to divalent manganese in acid solution by a reducing agent, such as divalent iron. The amount of permanganate can be determined by adding an excess of divalent iron and back titration with a standardized permanganate solution to a permanent faint pink color at the end-point.

Divalent manganese can be determined by oxidizing the manganese to permanganate with bismuthate in a cold acid solution. The permanganate formed can be determined after filtering off the excess bismuthate.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8\ H_2O$$

$$4MnSO_4 + 10NaBiO_3 + 14H_2SO_4 \longrightarrow 4NaMnO_4 + 5Bi_2(SO_4)_3 + 3Na_2SO_4 + 14H_2O$$

Solutions

Standardized potassium permanganate, 0.1 N.

Procedure - Analysis of Manganous Nitrate

Weigh accurately 1.2 g. of sample and place in a 250 ml. volumetric flask containing 200 ml. of water. After mixing, dilute to the mark and mix. Pipet a 20 ml. aliquot into a beaker and add 80 ml. of 3 N sulfuric acid. Add 1.0 g. of sodium bismuthate and agitate mixture for 1-2 min. After allowing the suspended bismuthate to settle, decant through a fine sintered glass filter (funnel type). Wash the filter and excess bismuthate with 3 N sulfuric acid until the washings passing through the filter are colorless. Using the filtrate, proceed as described under "General".

Procedure - Analysis of Potassium Permanganate

Dissolve 2.5-3.0 g. of accurately weighed sample in water. Transfer the solution to a 1 l. volumetric flask, dilute to the mark with water, and mix. Pipet a 10 ml. aliquot into an Erlenmeyer flask containing 100 ml. of water, and proceed as described under "General".

Procedure - General

Add 20 ml. of 0.1 N ferrous sulfate and 3 ml. of concentrated phosphoric acid to the permanganate solution and stir. Titrate the excess ferrous sulfate with standardized 0.1 N potassium permanganate solution to the appearance of a permanent faint pink color.

Carry a reagent blank through the general procedure, substituting 100 ml. of water for the sample.

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Calculations

$$\% \ KMnO_4 = \frac{(B-A) \times N \times 3.161}{\text{g. of sample in aliquot}}$$

$$\% \ Mn(NO_3)_2 = \frac{(B-A) \times N \times 3.579}{\text{g. of sample in aliquot}}$$

A = ml. of permanganate used to titrate sample
B = ml. of permanganate used to titrate blank
N = normality of permanganate solution.

References

1. Furman, "Scott's Standard Methods of Chemical Analysis", I, 5th Ed., D. Van Nostrand Co. (1939) pp. 474-571.

2. Hillebrand & Lundell, "Applied Inorganic Analysis", John Wiley & Sons, New York, (1929) pp. 343-6.

Written by: R. E. Ewing
Date: July, 1952

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DETERMINATION OF MANGANESE

Colorimetric Method

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Principle

This method is based on the oxidation of manganese to permanganate by periodate and the measurement of the intensity of the purple permanganate color, which is proportional to the concentration of manganese present. Only a small excess of periodate is needed for quantitative oxidation of manganese, although a large excess causes no harm. The reaction must be carried out in strongly acid solution to prevent precipitation of manganese as the insoluble iodate or periodate. For this purpose phosphoric acid is most effective.

Reducing agents, if present, should be oxidized by boiling with sulfuric and nitric acids (plus a little persulfate if carbon compounds are present); chloride ions should be removed by boiling to SO_3 fumes. A large excess of periodate will oxidize traces of such substances.

Tungsten, bismuth, and stannous ions cause turbidity; cupric, nickelous, cobaltous, chromic, and especially dichromate ions have interfering colors. The color due to ferric ions can be removed by phosphoric acid.

This procedure will determine manganese in the range 0.001 to 0.03%. Greater concentrations may be determined by using smaller samples, greater dilution, or absorption cells of shorter path length.

Solutions

Standard manganese solution, 0.3 g. Mn/l. Dissolve 0.1726 g. of $KMnO_4$ in exactly 200 ml. of solution.

Procedure - Analysis of Ferric Sulfate (Ferrifloc)

Weigh a 1.0 g. sample into a 100 ml. beaker. Add 25 ml. of water, 5 ml. of concentrated nitric acid, 5 ml. of concentrated phosphoric acid, and 0.2-0.4 g. of potassium periodate. Heat the solution just to boiling and allow it to simmer 10 min. If the permanganate color forms and then fades, add more periodate.

Cool the solution to room temperature, transfer it to a 50 ml. volumetric flask, and dilute to the mark with successive washings of the beaker (Remark 1).

Transfer a portion of the diluted solution into an absorption cell, having a path length of 5 cm. Measure the optical density at 525 and 545 millimicrons (Remark 2) with a Beckman spectrophotometer against a reference cell containing distilled water.

Determine the concentration of manganese, in ug./50 ml., from a standard curve prepared by running 0, 100, 200, 300, 500, 700, and 1000 ul. aliquots of the standard manganese solution through the above procedure.

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Calculations

$$\% \text{ Mn} = \frac{\text{ug. Mn}}{\text{g. sample}} \times 10^{-4}$$

Remarks

1. After a sample has been oxidized, make all further dilutions with water that has been distilled from an alkaline permanganate solution. Otherwise, color fading will occur due to oxidizable substances in the water.
2. The wave lengths of maximum absorption may vary somewhat with different instruments because of differences in the calibration and adjustment of the wave length scales. Consequently, the wave lengths at which the absorption peaks occur near 525 and 545 mu should be determined previous to preparing the first standard curve.

References

1. Willard, H.H., and Greathouse, L., Journ. Amer. Chem. Soc., 39, 2366 (1917).
2. Smith, G.F., "Analytical Applications of Periodic Acid and Iodic Acid and Their Salts", Ed. 5, G. F. Smith Chemical Co., Columbus, Ohio (1950).
3. Mehlig, Ind. Eng. Chem., Anal. Ed. 11, 274 (1939).

Written by: M. C. Lambert
Date: July, 1952

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DETERMINATION OF NITROGEN

Ammonia Distillation - Volumetric Method

Principle

Nitrogen is reduced by strong reductants to the negative trivalent form. Nitride nitrogen in metallic calcium is converted to ammonia in an alkaline medium. The ammonia is distilled into a boric acid solution, which is subsequently back-titrated to the original pH with standard acid to determine the ammonia.

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

$$H_2NH_4BO_3 + HCl \longrightarrow H_3BO_3 + NH_4Cl$$

Solutions

Standardized hydrochloric acid, 0.01 N.

Methyl red, 0.1%. 50 mg. per 50 ml. of absolute ethyl alcohol.

Bromcresol green, 0.1%. 50 mg. in 50 ml. of absolute ethyl alcohol.

Boric acid - indicator reagent; 20 g. of boric acid, 7.5 ml. of 0.1% bromcresol green solution, and 1.5 ml. of 0.1% methyl red solution in 1 l.

Procedure - Analysis of Calcium

Weigh 0.5 g. of calcium by difference and transfer it to a 100 ml. Kjeldahl flask. Connect the flask to a micro Kjeldahl distillation apparatus.

Place 5 ml. of the boric acid - indicator reagent in a 50 ml. Erlenmeyer flask and insert it under the end of the condenser tube, so that the exit is about 1/4" below the surface of the liquid.

Admit steam slowly to the distillation flask until the calcium is dissolved. Then, add 5 ml. of 50% sodium hydroxide solution and continue the steam distillation for 10 min., or until 20-25 ml. of distillate has been collected.

Remove the receiving flask and titrate with the standardized hydrochloric acid to the first tinge of red. Carry a blank through the entire procedure and titrate to an exactly matching color.

Calculations

$$\text{ppm N} = \frac{(A - B)\ C \times 0.014 \times 10^6}{\text{g. sample}}$$

A = ml. HCl to titrate sample
B = ml. HCl to titrate blank
C = normality of HCl

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Literature References

1. Niederl and Niederl, "Micromethods of Quantitative Organic Analysis", John Wiley and Sons, Inc., 69 (1947).

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Written by: A. H. Bushey
Date: July, 1952

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DETERMINATION OF NITROGEN COMPOUNDS

Nessler Method

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Principle

Nessler's reagent, K_2HgI_4, reacts in alkaline solution to give a pale yellow solution to a brown precipitate, depending on the concentration of ammonia. The test is delicate but is subject to interference from aldehydes, cyanides, sulfides, and bicarbonates.

The test may be applied to higher valent inorganic nitrogen compounds by making prior reduction with aluminum in alkaline medium.

$$NH_3 + 2K_2HgI_4 + 3KOH \longrightarrow NH_2IHg_2O + 7KI + 2H_2O$$

Solutions

Nessler's Reagent: weigh about 50 g. of KI into a 1 l. volumetric flask and dissolve in 35 ml. of water (Remark 1). Add saturated mercuric chloride ($HgCl_2$) solution slowly, and with stirring, till a slight red precipitate remains. Add about 400 ml. of 50% KOH solution, mix, and dilute to the mark with water. Allow to stand 24 hrs., then decant the clear liquid to a Pyrex container.

Standardized Ammonium Chloride, 0.01 mg. N per ml. Prepare a more concentrated solution by dissolving 3.818 g. of NH_4Cl with water to 1 l. in a volumetric flask. Dilute 10 ml. of this solution to 1 l.

Procedure - Analysis of Sodium Chloride and Potassium Chloride

Dissolve 2 g. ± 0.1 g. of sample in 40 ml. of water (Remark 1) in a 250 ml. Erlenmeyer flask. Add 10 ml. of 10% NaOH. Prepare a control containing 2 ml. of dilute ammonium chloride standard (0.01 mg. N per ml.) in 40 ml. of water. Add 10 ml. of 10% NaOH and proceed as under "General".

Procedure - Analysis of Oxalic Acid

Dissolve 2 ± 0.1 g. of sample in 20 ml. of water (Remark 1) in a 250 ml. Erlenmeyer flask. Add slowly, while cooling in an ice bath, 40 ml. of 10% NaOH.

Prepare a control containing 2 ml. of dilute ammonium chloride standard (0.01 mg. N per ml.), 20 ml. of water, and 40 ml. of 10% NaOH solution.

Dilute the sample and control solutions to about 100 ml. and continue as under "General".

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Procedure - Analysis of Chromium Nitrate

Dissolve 2.0 g. of sample in 20 ml. of water in a 100 ml. Kjeldahl flask. Assemble apparatus and add 5 ml. of 50% sodium hydroxide solution. Steam distill 50 ml. into 10 ml. of water containing 1 drop of conc. hydrochloric acid.

Dilute the distillate to 100 ml. in a volumetric flask. To a 50 ml. aliquot, add 5 ml. of 10% NaOH, 2 ml. of Nessler solution, and make up to the mark with water in a 100 ml. Nessler tube.

From a graduated pipet, transfer 2.4 ml. of standardized ammonium chloride (0.01 mg. N per ml.) to a 100 ml. Nessler tube. Add 5 ml. of 70% NaOH solution and 2 ml. of Nessler's reagent. Make to volume.

The color of the sample should be no darker than that of the reference.

Procedure - General

Add about 0.5 g. of C.P. Aluminum wire and stopper the flask with a one-hole stopper, containing a long glass vent tube, and allow to stand for 3 hrs. in an ammonia-free atmosphere. Decant one-half of the solution to a Nessler tube, add 2 ml. of Nessler's reagent, and compare the sample with the corresponding control. The color of the sample should be less than that of the control.

Remarks

1. It is essential that ammonia-free water be employed and that the test not be carried out in an atmosphere containing ammonia fumes.

Literature References

1. "Reagent Chemicals", American Chemical Society (1950).

2. McAlpine and Soule, "Prescott and Johnson's Qualitative Chemical Analysis", p. 425, D. Van Nostrand Co., Inc., New York (1933).

Written by: A. H. Bushey
Date: July, 1952

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DETERMINATION OF NITRITE

Oxidation Method

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Principle

Nitrite is determined by oxidation in acid solution to nitrate. Since nitrites are unstable in acid, an excess of oxidant is added immediately to the sample and the excess determined. Reducing agents other than nitrite in the sample interfere.

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5NaNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

$$5(NH_4)_2Fe_2(SO_4)_3 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5(NH_4)_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

The range is from 0 to 100%.

Solutions

Standardized potassium permanganate, 0.1 N.

Standardized ferrous ammonium sulfate, 0.1 N.

Preoxidized acidulated water. Add 20 ml. conc. H_2SO_4 to 1 l. distilled water and $KMnO_4$ to a persistent pink color (2 sec.)(about 10-15 drops 0.1 N).

Procedure - Analysis of Sodium Nitrite

Weigh accurately 1 g. of sample into a 100 ml. volumetric flask, dissolve in 20 ml. water, and dilute to the mark. Add from a buret 30 ml. of standard permanganate to 300 ml. of oxidized acidulated water and mix. Add slowly with rapid stirring and with the tip of the buret held under the surface of the liquid a 10 ml. aliquot of sample to the permanganate solution.

Allow to stand 5 min., then add 15 ml. of standardized ferrous ammonium sulfate, and allow to stand for 5 min. more. Titrate the excess reductant to a permanent pink color (2 sec.) with the $KMnO_4$ solution.

Calculations

$$\% \ NaNO_2 = \frac{(V_1 \times N_1) - (V_2 \times N_2) \times 0.0345 \times 100}{\frac{V_3}{V_4} \times W}$$

where V_1 = ml. of permanganate used
V_2 = ml. of ferrous ammonium sulfate
V_3 = ml. of aliquot
V_4 = ml. of sample dilution

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N_1 = normality of permanganate
N_2 = normality of ferrous ammonium sulfate
W_3 = weight of sample in grams.

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Literature References

1. Rosin, "Reagent Chemicals and Standards", p. 48, D. Van Nostrand Co., (1937).

Written by: W. N. Carson
Date: July, 1952

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DETERMINATION OF LOWER OXIDES OF NITROGEN

Permanganate Method

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Principle

For practical purposes the lower oxides of nitrogen in nitric acid may be determined volumetrically by titrating with standardized potassium permanganate. The oxides are calculated and expressed as nitrogen dioxide (NO_2).

$$5\ NO_2 + MnO_4^- + H_2O \longrightarrow 5\ NO_3^- + Mn^{++} + 2H^+$$

Solutions

Standardize potassium permanganate, 0.1 N.

Procedure - Analysis of Nitric Acid

Pipet 10 ml. of sample (Remark 1) into 150 ml. of water in a 250 ml. Erlenmeyer flask. Hold the pipet tip below the liquid surface during the addition and remove it just as the pipet empties.

Swirl the flask and titrate immediately with standardized 0.1 N potassium permanganate to a faint pink endpoint which persists for 30 seconds (Remark 2).

Calculations

$$\%\ NO_2 = \frac{V_1 \times N \times 4.6}{V_2 \times G}$$

N = normality of potassium permanganate
V_1 = ml. of potassium permanganate
V_2 = ml. of sample
G = specific gravity of sample.

Remarks

1. The sample weight is found from the volume and specific gravity of the sample.

2. The reaction may be slow near the endpoint, hence adequate time must be allowed for complete oxidation.

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", II, 5th Ed., D. Van Nostrand Co., Inc., New York, 2212 (1935).

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Date: July, 1952

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DETERMINATION OF NITRITE

Diazotization Method

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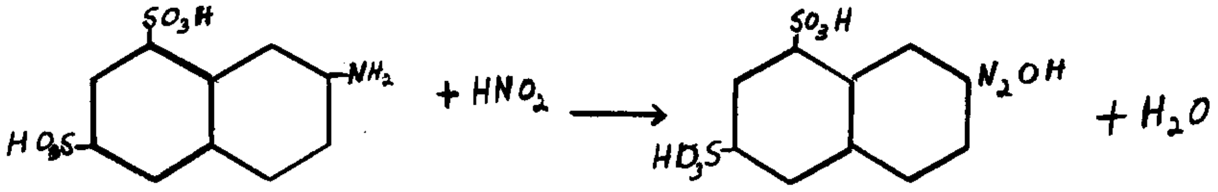
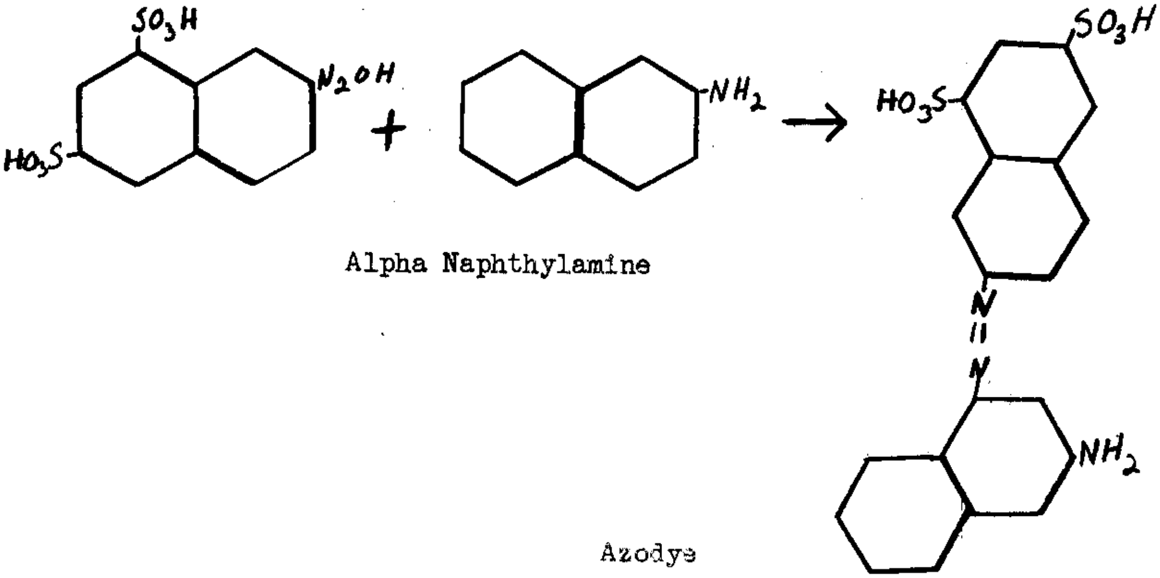
Principle

In the presence of aromatic amines, nitrite in acid solution is converted to diazonium salts, which can be coupled with aromatic amines to give intensely colored azodyes. By using an amine that does not couple to give dyes to make the diazonium salt, and then coupling with another aromatic amine, the amount of dye formed becomes stoichiometric with respect to nitrite.



Amino-G Acid

Diazotized Amino-G Acid



Alpha Naphthylamine

Azodye

Solutions

Standardized nitrite, 1 M. Dissolve approx. 70 g. of C.P. sodium nitrite in 1 liter of distilled water. Standardize against 0.1 N permanganate by adding an aliquot of nitrite solution to an excess of the standard permanganate in dilute acid, using care to prevent the decomposition of nitrite by the acid or air. Add standard ferrous ammonium sulfate solution in excess of remaining permanganate and back titrate excess ferrous with additional standard permanganate to a permanent pink (2 sec.) color.

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$$\underline{M}\ NO_2^- = \frac{(V_{MnO_4} \times N_{MnO_4}) - (V_{Fe} \times N_{Fe})}{2 \times \text{ml. of aliquot}}$$

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0.3% Amino-G acid solution. Dissolve 3 g. of amino-G acid (7 naphthylamine 1, 3 disulfonic acid) in 1 liter distilled water.

0.5% Alphanaphthylamine solution. Dissolve 5 g. of alphanaphthylamine (1 aminonaphthylamine) in 1 liter of distilled water.

Procedure - Analysis of Aluminum Nitrate

Weigh 1 g. sample and transfer to 25 ml. volumetric flask, rinsing in with distilled water. Add 1 ml. of 0.3% amino-G acid solution. Mix thoroughly and cool. Add 3 ml. of 0.5% alphanaphthylamine solution. Mix thoroughly and allow to stand 10 min. Prepare a blank in the same manner as the sample, using the same reagents, etc. Dilute sample and blank to the mark and mix thoroughly.

Read transmission of the sample on a Beckman DU Spectrophotometer at 438 mu against the reagent blank. Use appropriate size cell for the solution (1, 5, 10 cm.). Read the amount of nitrite from calibration curve.

Prepare calibration curve by using 5, 10, 15, 20 and 25 ul. aliquots of a standard 1 M sodium nitrite solution. Prepare blank and use procedure given for sample for color development. Plot on semi-log paper the transmission (ordinate-log scale) vs. ug. NO_2 (abscissa) and draw curve. The curve should pass through the 100% transmission, zero nitrite point. A new curve is required for each batch of reagents.

Calculations

$$\%\ NO_2^- = \frac{\text{ug. nitrite from curve} \times 100}{\text{g. sample} \times 10^6}$$

$$\text{ppm } NO_2 = \%\ NO_2^- \times 10^4.$$

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DETERMINATION OF NITRATE

Ferrous Sulfate Method

Principle

Ferrous sulfate reduces nitrate to nitric oxide in sulfuric acid medium; excess ferrous sulfate combines with the liberated nitric oxide to form a brown addition complex. The reaction is employed qualitatively as the basis of the familiar brown ring test. It may be employed for a colorimetric determination by making comparison with standards, or volumetrically by titrating with standard ferrous solution to the brown colored endpoint.

$$2NaNO_3 + 6FeSO_4 + 4H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Na_2SO_4 + 2NO + 4H_2O$$

$$FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$$

Solutions

Standardized ferrous sulfate, 0.5 N. Dissolve about 139 g. of $FeSO_4 \cdot 7H_2O$ in about 400 ml. of water and add 50 ml. of concentrated sulfuric acid. Cool and dilute to 1 l.

To standardize, dry "nitrometer standard", or recrystalized C.P. KNO_3 to constant weight at 135°C. Weigh and titrate a portion as described under "Procedure - Analysis of Sodium Nitrate".

$$N = \frac{W}{0.337 \times V}$$

W = g. of potassium nitrate
N = normality of ferrous sulfate
V = ml. of ferrous sulfate.

Standardized nitrate solution, 0.5 mg. HNO_3/ml. Measure 495 ml. of concentrated sulfuric acid with a graduate and transfer to a 600 ml. beaker in an ice bath. Add with a pipet exactly 5 ml. of a solution prepared by dissolving 8.022 g. of dried KNO_3 in exactly 100 ml. of aqueous solution; keep the pipet tip in constant motion during the addition.

Ferrous Sulfate, 0.2 M. Dissolve 27.8 g. of $FeSO_4 \cdot 7H_2O$ in 300 ml. of water. Add 150 ml. of sulfuric acid, cool, and make to 500 ml. Add a 1" piece of pure iron wire, hold the solution in an amber bottle, and do not keep for longer than one month.

Procedure - Analysis of Sulfuric Acid

Add 2 ml. of standardized nitrate solution (0.5 mg. HNO_3/ml.) to a 100 ml. Nessler tube.

With a Mohr pipet add 5.5 ml. (10 g.) of sulfuric acid sample to a second Nessler tube.

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To both solutions add 5 ml. of 0.2 M ferrous sulfate solution and make to 100 ml. with concentrated C.P. sulfuric acid.

The color produced in the sample should be less than that in the control.

Procedure - Analysis of Sodium Nitrate

Weigh exactly 0.12-0.14 g. of sample, dissolve it in 3-4 ml. of water, and add about 30 ml. of concentrated phosphoric acid.

Titrate with standardized 0.5 N ferrous sulfate solution (Remark 1) to the appearance of the first permanent yellowish-brown color.

$$\% \, NO_3 = \frac{V \times N \times 2.067}{W}$$

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V = ml. of ferrous sulfate
N = normality of ferrous sulfate
W = weight of sample.

Remark

1. The reaction of ferrous sulfate and nitrate undergoes an induction period that is retarded by an initial excess of ferrous ion. Therefore, add the first 0.5-1.0 ml. of reagent and stir until the reaction starts, as indicated by the gradual appearance of a dark brown color that fades suddenly.

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand Co., 2214-19 (1939).

Written by: A. H. Bushey
Date: July, 1952

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DETERMINATION OF NITRATE

Phenoldisulfonic Method

Principle

Phenoldisulfonic acid, $C_6H_3OH(SO_3H)_2$, reacts with nitrate to form a yellow, water soluble compound that can be employed as a basis for nitrate determination. Carbonate, chloride, nitrates, and organic matter constitute interferences.

Solutions

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1, 3, 5 phenoldisulfonic acid reagent, as purchased.

Standardized nitrate solution, 0.5 mg. NO_3/l. Dissolve 0.815 g. of KNO_3 in water and make to exactly 1 l.

Procedure

Dissolve a 0.5 g. sample in a small volume of water and make basic to pH paper with 1:1 ammonium hydroxide. Boil to a small volume and evaporate to dryness on a steam bath (Remark 1).

Add 2 ml. of phenoldisulfonic acid reagent to the dry sample and rub with a stirring rod to assure that the reagent contacts all the dried sample. Add 15 ml. of water and 1:1 ammonium hydroxide until the solution is strongly basic to pH paper and the yellow color develops.

Transfer the solution to a 50 ml. Nessler tube, filtering if necessary, and make to volume. Compare the sample color with that of a control containing 1 ml. of standard 0.5 mg/ml NO_3 solution.

Calculation

$$\% \; NO_3 = \frac{A \times B \times 100}{C}$$

A = ml. of nitrate standard
B = g/ml. of NO_3 in standard
C = g. of sample.

Remarks

1. Avoid overheating the sample to prevent volatilization of ammonium nitrate.

Literature References

1. Millan, "Organic Reagents in Inorganic Analyses", p. 480 (1941).

Written by: A. H. Bushey
Date: July, 1952

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DETERMINATION OF NITRATES AND CHLORATES

Diphenylamine Method, Qualitative

DECLASSIFIED

Principle

Diphenylamine is acted upon by chlorates and nitrates, as well as many other oxidizing agents, such as bromates, chromates, iodates, molybdates, permanganates, peroxides, and vanadates, to form successively the oxidation products diphenylbenzidine and diphenylbenzidine violet. The identifying color of the latter may be more readily recognized by allowing the reaction to take place at the liquid interface between the sample solution and sulfuric acid.

$$\underset{\text{(Diphenylamine)}}{C_6H_5{\cdot}NH{\cdot}C_6H_5} \longrightarrow \underset{\text{(Diphenylbenzidine)}}{C_6H_5\text{-}NH\text{-}C_6H_4\text{-}C_6H_4\text{-}NH\text{-}C_6H_5}$$

$$\longrightarrow \underset{\text{(Diphenylbenzidine violet)}}{C_6H_5\text{-}N{=}C_6H_4{=}C_6H_4{=}N\text{-}C_6H_5}$$

Solutions

Diphenylamine: dissolve 1 g. in 100 ml. of concentrated sulfuric acid.

Procedure - Analysis of Sodium Chloride and Potassium Chloride

Weigh approximately 1 g. of sample and dissolve in 10 ml. of water. Carefully overlay the solution on 10 ml. of diphenylamine solution. No blue ring should develop at the interface during a 20 min. period.

Procedure - Analysis of Barium Chloride

Weigh about 2 g. of sample. Dissolve in 20 ml. of water and add 1 ml. of concentrated sulfuric acid. Filter through a Whatman #40 paper and overlay 10 ml. of the filtrate on 10 ml. of diphenylamine solution. No blue ring should develop at the interface during a 20 min. period.

Literature References

1. "Specifications for Analytical Reagents", American Chemical Society, Washington, D.C., 87, March, 1941.

2. Mellan, "Organic Reagents in Inorganic Analysis", Blakiston, 478 (1941).

Written by: A. H. Bushey
Date: July, 1952

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DETERMINATION OF ALKALI METALS

Gravimetric Method

DECLASSIFIED

Principle

The sample is treated to remove the main constituent by precipitation. The filtrate containing the soluble alkali metal salts is evaporated to dryness and weighed.

Procedure - Analysis of Barium Chloride

Weigh accurately 5 g. of sample into a beaker and dissolve in 150 ml. of water. Add 1 ml. of concentrated hydrochloric acid and heat to boiling. Add 25 ml. of 1 M sulfuric acid and cool to room temperature. Transfer the solution and precipitate to a 250 ml. volumetric flask and dilute to the mark. After allowing to stand overnight, decant through a filter. Evaporate 100 ml. of the filtrate to dryness in a tared evaporating dish and ignite the residue at 900°C for 30 min. Cool and weigh.

The weight of the residue should not exceed the weight of a reagent blank by more than 1.0 mg.

Procedure - Analysis of Phosphoric Acid

Weigh accurately 3.0 g. of sample into a beaker. Add 100 ml. of water and 50 ml. of 30% lead acetate. Centrifuge the lead phosphate precipitate from the solution and decant the supernate through a filter, without washing the precipitate, into a graduate. Dilute to 200 ml. and mix.

Pipet 100 ml. of the tiltrate into an Erlenmeyer flask. Pass hydrogen sulfide through the solution until all of the lead is precipitated. Filter the solution into a tared evaporating dish containing 2 drops of concentrated sulfuric acid. Evaporate to dryness and ignite at 500°C for 1 hour. Cool and weigh.

The weight of the ignited residue should not exceed the weight obtained in a complete blank test with the lead acetate by more than 3.0 mg.

Reference

1. "Reagent Chemicals", American Chemical Society, Washington, D.C., (1950), p. 401.

Written by: R. E. Ewing
Date: July, 1952

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DETERMINATION OF ALKALI AND ALKALINE EARTHS

Gravimetric Method

DECLASSIFIED

Principle

After the interfering elements are removed, the sample is evaporated to dryness with excess sulfuric acid to yield a residue of the sulfates of the alkali and alkaline earth metals. All heavy metals interfere and must be removed.

Procedure - Analysis of Aluminum Nitrate Solution.

Evaporate a 3 g. sample twice with 7 ml. of HCl. Take up the residue in 50 ml. of hot water and pour the solution into a mixture of 10 ml. of NH_4OH and 70 ml. of water. Boil until nearly free from NH_3 odor, filter, and wash to 150 ml. Take a 50 ml. aliquot and follow the general procedure (Remark 1).

Procedure - Analysis of Chromium Nitrate

Dissolve 4 g. of chromium nitrate in 150 ml. of water. Add 15 ml. of concentrated ammonium hydroxide to precipitate the chromium. Boil to expel the excess ammonia, cool, filter, and dilute to 200 ml. Take a 50 ml. aliquot and follow the general procedure.

Procedure - Analysis of Cobalt Nitrate

Dissolve a 2 g. sample in 90 ml. of distilled water, add 2 ml. of HCl, and then make alkaline with NH_4OH. Pass in H_2S gas slowly for two minutes, dilute to 100 ml., mix, and filter through a dry filter paper. Take a 50 ml. aliquot and follow the general procedure below.

Procedure - General

Transfer the 50 ml. aliquot to a tared platinum dish, add 5 drops of H_2SO_4, and evaporate carefully to dryness. Ignite at 850-900°C, cool, and weigh. (Remark 2).

Calculations

$$\% \text{ Alkaline earths as sulfates} = \frac{\text{g. residue} \times 100}{\text{g. sample in aliquot}}$$

Remarks

1. The solution obtained at this point can be used for the sulfate determination as well as the alkaline earth determination.

2. Not more than 0.003 g. of residue should remain.

July, 1952

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References

1. Rosin, J., "Reagent Chemicals and Standards", D. Van Nostrand Co., Inc., p. 25, (1937).

2. ibid., p. 142.

Written by: R. J. Brouns
Date: July, 1952

[redacted]

DETERMINATION OF NICKEL

Gravimetric Method

DECLASSIFIED

Principle

Nickel is determined by weighing the bulky precipitate formed with dimethylglyoxime. The scarlet precipitate is formed in ammoniacal, neutral, or acetate-buffered solutions. It is soluble in mineral acids and organic solvents. Precipitation of iron, aluminum, and chromium complexes is prevented by the addition of tartrate or citrate. Large amounts of cobalt retard the precipitation of nickel because cobalt forms an orange-brown, soluble compound with dimethylglyoxime, and it is necessary to add sufficient reagent to combine with all of the cobalt to insure complete precipitation of the nickel. However, a large excess of reagent (more than 5% excess) should be avoided because dimethylglyoxime is not very soluble in water, and crystals of the reagent may separate out along with the nickel precipitate.

Procedure - Analysis of Cobalt Nitrate

Weigh a 1.0 g. sample, dissolve in 200 ml. of water, and add 2 g. of sodium tartrate. Heat to about 70°C and add 100 ml. of a 1% alcoholic solution of dimethylglyoxime. Add 5 ml. of ammonium hydroxide and allow the solution to stand overnight (Remark 1). Filter through a tared Gooch or fritted glass crucible. Wash thoroughly with cold water, dry at 110-120°C for 1 hr. or more, and weigh.

Calculations

$$\% \text{ Ni} = \frac{\text{g. precipitate} \times 20.32}{\text{g. sample}}$$

Remarks

1. If only a very small amount of nickel is present, the precipitate will probably be contamined with excess of oxime crystals. In that event, filter on paper and ash. Dissolve the ash in a small volume of 1:1 nitric acid, dilute with a little water and boil off oxides of nitrogen. Dilute to about 50 ml., add about 0.5 g. of sodium tartrate, heat to 70°C, and add only 2 ml. of a 1% alcoholic solution of the oxime. Make slightly ammoniacal and digest for an hour at 60-70°C. Cool, filter, dry at 110-120°C, and weigh.

References

1. Willard, H.H., and Diehl, H., "Advanced Quantitative Analysis", New York, D. Van Nostrand Co., pp. 71-73, 383-85 (1943).

Written by: M. C. Lambert
Date: July, 1952

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DETERMINATION OF HYDROGEN PEROXIDE

DECLASSIFIED

Ceric Oxidation - Volumetric Method

Principle

Hydrogen peroxide is oxidized quantitatively by ceric sulfate in a volumetric titration:

$$4Ce(HSO_4)_4 + 2H_2O_2 \longrightarrow 2Ce_2(SO_4)_3 + 2O_2 + 10H_2SO_4$$

Reducing agents interfere, if present, causing high results.

Solutions

Ceric sulfate, 0.1 N.

Ferroin indicator.

Procedure - Analysis of Hydrogen Peroxide

Weigh accurately 1-2.5 g. sample into a 500 ml. volumetric flask containing about 300 ml. distilled water and dilute to the mark, mixing well. Transfer a 25 ml. aliquot to an Erlenmeyer flask, acidify, and add 5 ml. excess 6 N sulfuric acid. Add one drop of ferroin indicator. Titrate with standardized 0.1 N ceric sulfate solution to a pale blue endpoint.

Calculations

$$\% \; H_2O_2 = \frac{\text{ml. standard ceric x normality x 1.701}}{\text{g. sample in aliquot}}$$

References

1. Oesper, "Newer Methods of Volumetric Analysis", D. Van Nostrand, 44 (1938).

Written by: U. L. Upson
Date: July, 1952

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DETERMINATION OF WATER

Distillation Method

DECLASSIFIED

Principle

Water may be removed from a variety of materials by boiling them with solvents, such as benzene (C_6H_6), toluene (C_7H_8), and xylene (C_8H_{10}), all of which are immiscible with water. If the distillate is collected, the water and solvent separate into two phases. If the collector is graduated, the amount of water may be read directly. Toluene or xylene are generally used as the organic solvents.

Apparatus

Dean and Stark water test apparatus, A.S.T.M. Designation D95.

Procedure - Analysis of Barium Chloride, Ceric Ammonium Nitrate, Potassium Chloride, Sodium Chloride, and Sodium Nitrite

Weigh 100 g. of sample and place in the distilling flask. Add 100 ml. of toluene or xylene to the flask and assemble the apparatus. Heat the flask, regulating the temperature so that the distillation proceeds at a rate of 2-5 drops per second. Continue the distillation until the water level in the trap remains constant and read this level. Determine a reagent blank on each batch of solvent used.

Calculations

$$\% \text{ water} = \frac{(A - B) \times 100}{C}$$

A = g. of water collected
B = g. of water in an equal volume of blank
C = wt. of sample in g.

Remarks

1. If water content of a sample is believed to be greater than 10%, a proportionally smaller sample size should be used.

References

1. A.S.T.M. Standards, Part III, Designation D95-40, American Society for Testing Materials, Philadelphia, Pa., 262-265 (1942).

Written by: W. G. Burch
Date: July, 1952

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DETERMINATION OF WATER

Qualitative Method

DECLASSIFIED

Principle

The presence of water in many materials may be detected by its producing a cloudy appearance.

Procedure - Analysis of Tributylphosphate

Measure 38 ml. of white gasoline (60° Baume'- Sp.Gr. 0.745) into a flask equipped with a stirrer and maintained at 20°C in a constant temperature bath. Add 2 ml. of sample and stir. If water is present, turbidity will result.

Procedure - Analysis of Trichlorethylene

Measure approximately 20 ml. of the sample and transfer to a 50 ml. test tube. To a 400 ml. beaker add 200 ml. of acetone and cool the acetone to -10°C by dropping in small pieces of dry ice. Immerse the test tube containing the sample into the cold acetone long enough to be cooled to -10°C, then remove the sample and allow to stand until room temperature is reached. Any resulting cloudiness or turbidity indicates a suspension of water.

Written by: W. G. Burch
Date: July, 1952

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DETERMINATION OF WATER
(By Dehydration)

DECLASSIFIED

Principle

The hydroscopicity of many materials may be determined by the dehydration of the parent material.

Procedure - Analysis of Sodium Pyrophosphate

Weigh accurately about 2 grams and ignite at a low red heat in a weighed desiccating dish. Cool in a desiccator and reweigh to determine the percentage of water.

Reference

Furman, "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand, 1939.

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DETERMINATION OF PHOSPHATE

DECLASSIFIED

Colorimetric Method

Principle

Phosphates in dilute mineral acid solution react with molybdates to form molybdiphosphoric acid. This acid is extractable in certain organic solvents including butanol - 1. The extracted acid may be reduced with stannous chloride to give molybdenum blue. The intensity of the color of the alcoholic molybdenum blue solution is measured at 735 mu.

Silicates, arsenates, and germanates will give a similar test. If the extraction of molybdiphosphoric acid by butanol - 1 is carried out from solution 1 N in sulfuric acid, molybdisilicic acid and molybdigermanic acid are not extracted.

$$24\ H^{+} + PO_4^{-3} + 12\ MoO_4^{-2} \longrightarrow P(Mo_3O_{10})_4^{-3} + 12\ H_2O$$

$$P(Mo_3O_{10})_4^{-3} + Sn^{+2} \longrightarrow Sn^{+4} + \text{molybdenum blue}$$

Solutions

Standard phosphate solution, 0.20 g. of phosphate/l. Weigh accurately 0.2866 g. of KH_2PO_4, dried 6-12 hours at 100-105°C, into a one liter volumetric flask. Dilute to mark with distilled water.

Ammonium molybdate solution, 6.25%. Dissolve 62.5 g. of ammonium molybdate in 900 ml. of redistilled water heated to 50°C. Transfer solution to a 1 liter volumetric flask and dilute to mark with redistilled water.

Stannous chloride solution, 40%. Dissolve 200 g. of $SnCl_2$ in 300 ml. of conc. HCl. Dilute to 500 ml. with conc. HCl.

Procedure - Analysis of Potassium Chloride

Weigh accurately about 1 g. of sample and proceed as described in the general procedure.

Procedure - Analysis of Sodium Chloride

Weigh accurately about 4 g. of sample and proceed as described in the general procedure.

Procedure - General

Add sample to 7.0 ml. of water and 1.0 ml. of 10 N sulfuric acid in a 125 ml. separatory funnel. Add 2.0 ml. of ammonium molybdate solution, mix and allow to stand for 5 minutes. Add 9.0 ml. of butanol - 1 and agigate for 2 minutes. Discard the aqueous layer. Wash the organic phase with two 5.0 ml. portions of 1 N sulfuric acid. Add 75 ul. of stannous chloride solution and 15 ml. of 1N sulfuric acid, agitate, allow to settle and discard aqueous phase.

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Transfer alcoholic solution to a 10 ml. volumetric flask and dilute to mark with 95% ethanol. Compare against reagent blank in the spectrophotometer at 735 mu wavelength.

Compare the transmittancy against the transmittancy obtained by carrying 5, 10, 25, 50, and 100 ul. of the standard phosphate solution through the same procedure.

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Calculations

$$\%\ PO_4 = \frac{g.\ PO_4}{g.\ sample}$$

$$ppm\ PO_4 = \%\ PO_4 \times 10^4$$

Remarks

A new calibration curve or factor should be determined whenever a new phosphate standard, molybdate solution, or butanol - 1 are introduced into the procedure.

Literature References

1. Buenblum and Chnin, Biochem. J., 32, 295 (1938).
2. Fish, Rasmussen, Kitson, and Kirk, CN Report No. 1791.

Written by: Jeanette Watkins
Date: July 1952

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DETERMINATION OF PYROPHOSPHATE

Potentiometric Method

DECLASSIFIED

Principle

Tetra sodium pyrophosphate is converted to the dihydrogen salt at pH 3.8. Addition of zinc sulfate precipitates zinc pyrosulfate and liberates sulfuric acid. The acid is titrated potentiometrically with standard caustic. The method is not accurate in the presence of polyphosphates.

$$Na_4P_2O_7 + 2HCl \longrightarrow Na_2H_2P_2O_7 + 2\ NaCl$$

$$Na_2H_2P_2O_7 + 2ZnSO_4 \longrightarrow Zn_2P_2O_7 + Na_2SO_4 + H_2SO_4$$

Solutions

Standard sodium hydroxide, 0.25 N. Titrate 1 g. of dry C.P. $Na_4P_2O_7$ according to the procedure.

$$A = \frac{\text{g. C.P. } Na_4P_2O_7}{\text{ml. NaOH}}$$

A = $Na_4P_2O_7$ equivalent of NaOH.

Procedure - Analysis of Sodium Pyrophosphate

Weigh accurately about 1 g. of sample and dissolve in sufficient distilled water so that the solution will just cover the electrodes of a pH meter. Adjust the pH of the solution to exactly 3.8 by adding 0.25 N hydrochloric acid. Add 50 ml. of 10% zinc sulfate solution and allow about 5 min. for the reaction to become complete, as shown by the pH becoming constant.

Titrate the liberated sulfuric acid with 0.25 N standard sodium hydroxide until a pH of 3.8 is again reached.

Calculations

$$\%\ Na_4P_2O_7 = \frac{A \times B \times 100}{W}$$

A = $Na_4P_2O_7$ equivalent of NaOH
B = ml. of 0.25 N NaOH required for titration
W = g. of sample.

References

1. "American Society for Testing Materials Standards", III American Society for Testing Materials, Philadelphia 1536, 1542 (1942).

Written by: W. G. Burch
Date: July, 1952

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DETERMINATION OF LEAD

Electrodeposition Method

DECLASSIFIED

Principle

Lead is deposited on an anode as PbO_2 when the current is controlled between 0.5 to 1.0 amps, at 2.0 to 2.5 volts, while copper is simultaneously deposited on the cathode. Control of acidity is likewise required when interfering elements are present.

Apparatus

"Slomin" electrolytic apparatus.

Procedure - Analysis of Pb in Tin

Dissolve a weighed 0.1 g. sample in 1:1 nitric acid. Transfer the solution to a large, tared platinum dish. Add 20-25 ml. of concentrated nitric acid and dilute the solution to a volume of 150 ml. Electrolyze the cold solution, using the metal dish as anode and a platinum spiral wire or gauze as cathode, at least three hours. Longer periods are advisable if current strength is decreased to 0.05 amp.

Electrolysis is complete when no further deposition is observed after the addition of sufficient water to cover an additional portion of the dish. The dish is dried at 220°C and weighed.

Calculations

$$\% \text{ Pb} = \frac{\text{g. } PbO_2 \times 0.8643 \times 100}{\text{g. of sample}}$$

References

1. Scott's Standard Methods of Analysis, 5th Ed., Vol. 1, p. 507-8.

Written by: W. W. Mills
Date: July, 1952

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DETERMINATION OF HEAVY METALS

Hydrogen Sulfide Method

DECLASSIFIED

Principle

Hydrogen sulfide is passed through a slightly acidic solution of the sample and the metal sulfide color is compared with a control containing the maximum permissible amount of heavy metals as lead. The solution is made alkaline to detect iron. This evaluation will indicate whether the heavy metal content is above or below the maximum permissible limit.

$$Pb(CH_3COO)_2 + H_2S \longrightarrow PbS + 2CH_3COOH$$

Solutions

Phenolphthalein, 1%. Dissolve 1 g. in 100 ml. of 95% ethyl alcohol.

Standardized lead solution, 0.1 mg. Pb/ml. Dissolve 0.1599 g. of anhydrous lead nitrate in 1 l. of water.

Procedure - Analysis of Aluminum Nitrate Solution

Weigh 2.5 g. of solution and proceed as described under "General". Maximum permissible is 0.004%.

Procedure - Analysis of Nitric Acid

Weigh 10 g. of solution and proceed as described under "General", using 0.5 ml. of lead standard instead of 1 ml. Maximum permissible is 0.0005%.

Procedure - Analysis of Sulfamic Acid

Weigh 1 g. of sample and proceed as described under "General". Maximum permissible is 0.01%.

Procedure - Analysis of Hydrofluosilicic Acid

Weigh 2 g. of sample and proceed as described under "General". Maximum permissible is 0.005%.

Procedure - Analysis of Barium Chloride

Dissolve 2 g. of sample in 20 ml. of water and add 2 drops of concentrated hydrochloric acid. Saturate the solution with hydrogen sulfide. Add 2 ml. of concentrated ammonium hydroxide. If no darkening is observed either before or after the addition of ammonium hydroxide, report heavy metals as less than 0.0005% lead and less than 0.0002% iron.

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Procedure - Analysis of Oxalic Acid

Dissolve 2 g. of sample in 50 ml. of water and saturate with hydrogen sulfide. Add 2 ml. of concentrated ammonium hydroxide. If no darkening is observed either before or after the addition of ammonium hydroxide, report heavy metals as less than 0.0005% lead and less than 0.0002% iron.

Procedure - General

Place the weighed sample in a 100 ml. Nessler tube containing 60 ml. of distilled water. Add 2 drops of phenolphthalein and neutralize to a pale pink color by adding concentrated ammonium hydroxide. Add 1 ml. of glacial acetic acid and dilute to 100 ml. with distilled water. Mix thoroughly.

Place 1 ml. of lead solution and 1 ml. of glacial acetic acid in a 100 ml. Nessler tube containing 60 ml. of distilled water. Dilute to 100 ml. with distilled water. Mix thoroughly.

Bubble hydrogen sulfide gas through both solutions for 5 min. If the sample is lighter than the standard, report the heavy metal content as less than the maximum permissible limit.

Literature References

1. Rosin, "Reagent Chemicals and Standards", 321, D. Van Nostrand Co., Inc., New York, 1939.

2. American Chemical Society, "Specifications for Analytical Reagents", American Chemical Society, Washington, 1941.

Written by: H. H. Van Tuyl
Date: July, 1952

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DETERMINATION OF SULFITE

DECLASSIFIED

Volumetric Method

Principle

A weighed sample reacts with a known excess of iodine in acid solution. The excess iodine is titrated with sodium thiosulfate, using starch indicator. The amount of iodine which reacted with the sample is used to calculate the amount of sulfite present.

Any substances, other than sulfite, which can reduce iodine to iodide will interfere.

$$SO_3^{=} + I_2 + H_2O \longrightarrow SO_4^{=} + 2HI$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Solutions

Standardized iodine, 0.1 N.

Standardized sodium thiosulfate, 0.1 N.

Procedure - Analysis of Ammonium Sulfite

Weigh accurately 0.2 g. of sample into an iodine flask. Proceed as described under general procedure.

Procedure - Analysis of Sodium Sulfite

Weigh accurately 0.25 g. of sample into a glass stoppered flask. Proceed as described under general procedure.

Procedure - General

Add about 10 ml. of distilled water, 50 ml. of standardized 0.1 N iodine solution, and 5 ml. of conc. hydrochloric acid. Titrate with standardized 0.1 N sodium thiosulfate solution until the brown color is a light yellow. Add 1 ml. of 1% starch indicator solution and titrate to disappearance of the blue color.

Run a blank on the iodine solution, using the same amounts of all reagents, but omitting sample.

Calculations

$$\% \ (NH_4)_2SO_3 \cdot H_2O = \frac{(\text{ml. blank - ml. sample titration}) \times \text{N. thiosulfate} \times 6.708}{\text{g. sample}}$$

$$\% \ Na_2SO_3 = \frac{(\text{ml. blank - ml. sample titration}) \times \text{N. of thiosulfate} \times 6.303}{\text{g. sample}}$$

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References

1. Furman, Scott's Standard Methods of Chemical Analysis", I, 5th ed., D. Van Nostrand, N.Y., 926 (1936).

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Written by: M. B. Leboeuf
Date: July, 1952

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DETERMINATION OF SULFATE

Gravimetric Method

DECLASSIFIED

Principle

Sulfate is determined by precipitation and weighing of the insoluble barium salt. Sulfur may also be determined in this manner by prior treatment with HNO_3 to oxidize the sulfur to sulfate. Pb, Sr and Ca interfere due to the insolubility of their sulfates. Excessive quantities of Al, Fe, $CrO_4^{=}$, Cl^-, NO_3^-, ClO_3^-, and other ions interfere due to adsorption or occlusion in the $BaSO_4$ precipitate. The solubility of $BaSO_4$ is 3.9 mg. per liter at 100°C. For this reason, washing of the precipitate must not be excessive. Reagent blanks should be run frequently and results corrected when these blanks are found to be significant.

Procedure - Analysis of Sodium Nitrate

Dissolve a 10 g. sample, using 200 ml. of distilled water in a 600 ml. beaker. Add conc. HCl until the solution is neutral to methyl orange and add 2 ml. in excess. Heat the solution to boiling and add 100 ml. of boiling, 1% $BaCl_2$ solution, while stirring. Proceed as described under "General". Report as percent SO_4. Gravimetric Factor = 0.4115.

Procedure - Analysis of Sodium Sulfite

Dissolve a 1 to 2 g. sample, using 200 ml. of distilled water in a 400 ml. beaker. Add 10 ml. of conc. HCl and boil vigorously until SO_2 evolution ceases, as determined by bleaching effect of SO_2 on litmus paper. Dilute the solution to 200 ml., heat to boiling, and add 100 ml. of boiling, 1% $BaCl_2$ solution, while stirring. Proceed as described under "General". Report as percent Na_2SO_4. Gravimetric Factor = 0.6086.

Procedure - Analysis of Ammonium Sulfate

Dissolve a 5 g. sample in a 500 ml. volumetric flask, using distilled water. Dilute to the mark, mix quantitatively, and transfer an accurate 10 ml. aliquot to a 600 ml. beaker, containing 250 ml. of water. Add conc. HCl until the solution is neutral to methyl orange plus 2.5 ml. excess. Heat to boiling and add 100 ml. of boiling, 1% $BaCl_2$ solution, while stirring. Proceed as described under "General". Report as percent $(NH_4)_2SO_4$. Gravimetric Factor = 0.5661.

Procedure - Analysis of Cobaltous Nitrate

Dissolve a 5 g. sample in a 400 ml. beaker, using 10 ml. of hot, distilled water. Add 10 ml. of conc. HCl and evaporate the solution to dryness on a steam bath. Dissolve the residue in 5 ml. of water and 5 ml. of conc. HCl and re-evaporate the solution to dryness. Re-dissolve the residue in 2 ml. of conc. HCl and 200 ml. of water. If any insoluble material remains, filter the solution quantitatively into a 400 ml. beaker, using 0.05 N HCl as wash. Heat the solution to boiling and add 100 ml. of boiling, 0.1% $BaCl_2$ solution, while stirring. Proceed as described under "General". Report as percent SO_4. Gravimetric Factor = 0.4115.

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Procedure - Analysis of Sodium Dichromate

One gram of sample is dissolved in approximately 30 ml. of distilled water. One ml. of 6 N HCl and 10 ml. of 10% barium chloride solutions are added. The solution is brought to volume in a 100 ml. Nessler tube and compared with a second Nessler tube containing a standard dichromate solution to which 5 ml. of 0.001 g/ml of standard sulfate has been added. The sulfate is reported as greater or less than 0.5%, depending on turbidity.

Procedure - Analysis of Chromic Nitrate

Convert a 5 g. sample to the chloride by the procedure described under "Analysis of Cobaltous Nitrate". When the conversion is complete and the residue re-dissolved in 2 ml. of conc. HCl and 200 ml. of water, proceed with the addition of 2.5 ml. of 10% $BaCl_2$ solution as described under the "Analysis of Sodium Dichromate" and follow this procedure to completion. Report as per cent SO_4. Gravimetric Factor = 0.4115.

Procedure - Analysis of Bismuth

Dissolve a 5 g. sample in a 400 ml. beaker, using 60 ml. of conc. HNO_3. Boil the solution to insure complete dissolution of all soluble material and add 100 ml. of 10% HNO_3. Filter the solution through a sintered-glass filter to remove any insoluble, using 10% HNO_3 as a wash. Heat the solution to boiling and add 100 ml. of 0.1% $BaCl_2$ solution, while stirring. Proceed as described under "General", using 10% HNO_3 as the wash in place of hot water. Report as per cent S. Gravimetric Factor = 0.1373.

Procedure - Analysis of Coal

Place approximately 3 g. of Eschkas mixture in a 30 ml. porcelain crucible. Add 1000 g. of the 60 mesh, previously dried, coal sample and mix thoroughly with a glass stirring rod. The mixture which adheres to the stirring rod should be dusted into the crucible with a camel's hair brush. Cover the mixture with approximately 1 g. of Eschkas mixture. Place the crucible containing the mixture in a <u>cool</u> muffle furnace. Adjust the rheostat so that the temperature will rise rapidly to 800 to 825°C and ignite at the above temperature for 2-3 hrs.

Allow the crucibles to cool to room temperature. Stir the mixture with a glass rod. If black particles are present, the samples should be reignited at the above temperature until the coal is completely ashed.

September, 1953

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Procedure - Analysis of Sodium Dichromate

Dissolve a 100 g. sample in a 400 ml. beaker, using 250 ml. of distilled water. Add 0.5 ml. of conc. HCl, heat to boiling, and add 2.5 ml. of 10% $BaCl_2$ solution dropwise, while stirring. Digest on a steam bath for one hour and allow to stand until cool. Transfer the precipitate, quantitatively, to filter paper, wash with minimum quantity of hot water, transfer filter paper to a platinum crucible, and consume paper by ignition. Fuse the $BaSO_4$ precipitate with 3-5 g. of Na_2CO_3 in the platinum crucible. Extract Na_2SO_4 from the melt by dissolving in small volume of water. Filter the dissolved melt and wash residue with hot water. Neutralize the filtrate to methyl orange, using conc. HCl, and add 3 ml. in excess. Dilute to 200 ml. with distilled water, add 10 ml. of ethanol, and digest on a steam bath until the solution is colorless or a clear green. Neutralize the solution with conc. NH_4OH and add 2 ml. of conc. HCl. Heat to boiling and add 100 ml. of boiling, 0.1% $BaCl_2$ solution, while stirring. Proceed as described under "General". Report as percent Na_2SO_4. Gravimetric Factor = 0.6086.

Procedure - Analysis of Chromic Nitrate

Convert a 5 g. sample to the chloride by the procedure described under "Analysis of Cobaltous Nitrate". When the conversion is complete and the residue re-dissolved in 2 ml. of conc. HCl and 200 ml. of water, proceed with the addition of 2.5 ml. of 10% $BaCl_2$ solution as described under the "Analysis of Sodium Dichromate and follow this procedure to completion. Report as percent SO_4. Gravimetric Factor = 0.4115.

Procedure - Analysis of Bismuth

Dissolve a 5 g. sample in a 400 ml. beaker, using 60 ml. of conc. HNO_3. Boil the solution to insure complete dissolution of all soluble material and add 100 ml. of 10% HNO_3. Filter the solution through a sintered-glass filter to remove any insoluble, using 10% HNO_3 as a wash. Heat the solution to boiling and add 100 ml. of 0.1% $BaCl_2$ solution, while stirring. Proceed as described under "General", using 10% HNO_3 as the wash in place of hot water. Report as percent S. Gravimetric Factor = 0.1373.

Procedure - Analysis of Coal

Place approximately 3 g. of Eschkas mixture in a 30 ml. porcelain crucible. Add 1000 g. of the 60 mesh, previously dried, coal sample and mix thoroughly with a glass stirring rod. The mixture which adheres to the stirring rod should be dusted into the crucible with a camel's hair brush. Cover the mixture with approximately 1 g. of Eschkas mixture. Place the crucible containing the mixture in a cool muffle furnace. Adjust the rheostat so that the temperature will rise rapidly to 800 to 825°C and ignite at the above temperature for 2-3 hrs.

Allow the crucibles to cool to room temperature. Stir the mixture with a glass rod. If black particles are present, the samples should be re-ignited at the above temperature until the coal is completely ashed.

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Transfer the mixture quantitatively to a 600 ml. beaker, using hot water as the wash. Add enough hot distilled water to each beaker to make the volume approximately 200 ml. Digest the mixture on a steam bath for forty-five min. Filter the clear liquid through Whatman No. 40 filter paper and wash the insoluble matter by decantation with hot water. After several washings in this manner, transfer the insoluble matter to the filter and wash at least five times, keeping the volume of the filtrate below 400 ml.

To the clear filtrate add 10-20 ml. of a saturated solution of bromine water. Make the solution slightly acid by addition of 1:1 hydrochloric acid. Boil the solution until the liberated bromine is expelled, checking at regular intervals for the presence of bromine by adding one drop of a solution of methyl orange indicator. If bromine is present, the color will fade; if absent, a permanent pink color results. Neutralize the solution to the methyl orange endpoint, using a clear solution of sodium carbonate. Add 2 ml. of 1 N HCl. Place on a hot plate and boil to expel the liberated carbon dioxide. Add 10 ml. of boiling, 10% $BaCl_2$ solution, while stirring. Proceed as described under "General". Report as percent S. Gravimetric Factor = 0.1373.

Procedure - Analysis of Sodium Sulfate

Dry about 1.5 g. of sample at 100° in a porcelain dish. Ignite to constant weight at 400°C. Weigh accurately 0.4 g. of the ignited sample into a beaker and dissolve with 200 ml. of water and 1 ml. of concentrated hydrochloric acid. Heat to boiling and add 100 ml. of boiling 1% barium chloride, while stirring. Proceed as described under "General". Report as percent Na_2SO_4. Gravimetric Factor = 0.6086.

Procedure - General

Digest the precipitate on a steam bath for 1 hr., and allow to cool. Transfer the precipitate quantitatively to a tared Selas crucible. Wash the precipitate with a minimum volume of hot water until 25 ml. of washings give only a slight opulescence when tested for chloride ion, using $AgNO_3$ solution. Dry the crucible in an oven at 110°C and ignite in a muffle at 900°C for 30 min. Weigh.

Calculations

$$\%\ \text{Constituent Reported} = \frac{\text{Wt. of } BaSO_4 \text{ x Grav. Factor for constituent x } 100}{\text{Wt. of sample analyzed}}$$

Written by: D. G. Miller
Date: July, 1952

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DETERMINATION OF SULFATE

Volumetric Method

DECLASSIFIED

Principle

The sample is dissolved by treatment with hydrochloric acid in a reducing medium. The hydrogen sulfide gas evolved by this treatment is collected in an ammoniacal cadmium chloride solution by precipitation of CdS. The CdS is then treated with HCl, and the resulting H_2S is titrated with standard iodine solution.

Solutions

Standard Iodine Solution, 0.1 N.
Ammoniacal $CdCl_2$ - 1 g. $CdCl_2$, 40 ml. H_2O, 60 ml. conc. NH_4OH.

Procedure - Analysis of Tin

Place a 5 g. sample in a 500 ml. Erlenmeyer flask and add 1-2 g. of 20 mesh Zn metal. Provide the flask with a long-stem thistle tube and a tube through which the evolved gas may pass to a 250 ml. Erlenmeyer. Place 50 ml. of ammoniacal $CdCl_2$ solution in the second flask. Place the tip of the gas delivery tube well under the surface of the $CdCl_2$ solution. Make certain that the system is air-tight. Add 100 ml. of 6 N HCl through the thistle tube and allow the reaction to subside. Heat the sample flask to boiling for 20 min. Disconnect the gas delivery tube and discontinue heating. Rinse the delivery tube with distilled water, collecting the rinsings in the $CdCl_2$ flask and allow to cool. Transfer the cool solution to a 600 ml. beaker containing 275 ml. of water. Rinse the flask with water and 6 N HCl. Neutralize any excess NH_4OH with conc. HCl and add 10 ml. excess. Add 5 ml. of 0.5% starch solution and immediately titrate with standard iodine.

Calculations

$$\% \text{ Sulfur} = \frac{\text{ml. iodine} \times \text{normality} \times 1.6}{\text{wt. of sample}}$$

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis", 5th Ed., II, D. Van Nostrand Co., Inc., New York, 1442 (1939).

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Date: July, 1952

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DETERMINATION OF SULFATE

Turbidimetric Method

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Principle

The turbidity produced by the formation of insoluble $BaSO_4$ upon the addition of $BaCl_2$ to a solution containing the sulfate ion is visually compared with a standard. Pb, Sr, and Ca interfere due to the insolubility of their sulfates. Reagent blanks should be run and results corrected when these blanks are found to be significant.

Solution

Standard sulfate solution, 0.1 mg sulfate/ml. Weigh accurately 1.8140 g of potassium sulfate, which has been previously dried at 110° C for 1 hr. into a 1 l. volumetric flask. Dissolve with 100 ml of water and dilute to the mark. Mix thoroughly before using.

Procedure - Analysis of Aluminum Nitrate Solution

Weigh accurately 5 g of sample into a beaker. Add 7 ml of concentrated hydrochloric acid and evaporate to dryness on a steam bath. Repeat evaporation to dryness with 7 ml of concentrated hydrochloric acid. Dissolve the residue in 50 ml of hot water and pour into 80 ml of 2 M ammonium hydroxide. Boil off excess ammonia. Filter and wash precipitate with water until total volume of filtrate and washings is 200 ml. Transfer a 25 ml aliquot of the solution to a Nessler tube and neutralize with 1 N HCl. Proceed as described under "General".

Procedure - Analysis Chromium Nitrate

A five gram sample is made basic with NaOH and oxidized to Na_2CO_4 with 30% hydrogen peroxide. The sample is acidified with HCl and the sulfates are precipitated with Barium Chloride. Resulting turbidity is compared with standards in Nessler tubes.

Procedure - Analysis of Nitric Acid

Weigh accurately a 10 g sample into an evaporating dish and add 0.1 g of solid Na_2CO_3. Evaporate to dryness on a steam bath and dissolve the residue with 30 ml of water. Transfer the solution to a Nessler tube and proceed as described under "General".

Procedure - Analysis of Phosphoric Acid

Weigh accurately a 3 g sample into a Nessler tube containing 30 ml of water. Add conc. ammonium hydroxide until the solution is brought to a pH of 3-5. Proceed as described under "General".

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Procedure - Analysis of Hydriodic Acid

Weigh accurately a 3 g sample into an evaporating dish, add 0.1 g of sodium carbonate, and evaporate to dryness on a steam bath. Dissolve the residue in 30 ml of distilled water, transfer to a Nessler tube, and proceed as described under "General".

Procedure - Analysis of Oxalic Acid

Weigh accurately a 2 g sample in a platinum dish and dissolve with 20 ml of water. Add 10 mg of sodium carbonate and evaporate to dryness on a steam bath. Ignite to decompose the acid and dissolve the residue in 25 ml of water. Add 3 ml of saturated bromine water and heat on steam bath for 15 minutes. Neutralize the solution with conc. HCl. Boil to remove the bromine and filter. Dilute the filtrate to 25-50 ml, transfer to a Nessler tube, and proceed as described under "General".

Procedure - Analysis of Potassium Chloride and Soidum Chloride

Weigh accurately a 10 g sample into a Nessler tube and dissolve with 30 ml of water. Proceed as described under "General".

Procedure - Analysis of Hydrofluosilicic Acid

Evaporate a 1 g sample in a platinum dish on a steam bath with 1 ml of HF. Moisten the residue with 5 drops of conc. HCl and add 30 ml of distilled water. Filter, transfer to a Nessler tube, and proceed as described under "General".

Procedure - Analysis of Sodium Dichromate

One gram of sample is dissolved in approximately 30 ml of distilled water. One ml of 6 N HCl and 10 ml of 10% barium chloride solutions are added. The solution is brought to volume in a 100 ml Nessler tube and compared with a second Nessler tube containing a standard dichromate solution to which 5 ml of 0.001 g/ml of standard sulfate has been added. The sulfate is reported as greater or less than 0.5% depending on turbidity.

Procedure - General

Add 1 ml of 6 N HCl and 5 ml of 10% barium chloride solution. Dilute to 50 ml with distilled water and mix well. To a second Nessler tube, add 30 ml of distilled water, 1 ml of 6 N HCl, 5 ml of 10% barium chloride solution, and dilute to 50 ml with distilled water. To this second tube, add from a buret enough standard sulfate solution to match the turbidity in the sample tube.

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Procedure - Analysis of Oxalic Acid

Weigh accurately a 2 g. sample in a platinum dish and dissolve with 20 ml. of water. Add 10 mg. of sodium carbonate and evaporate to dryness on a steam bath. Ignite to decompose the acid and dissolve the residue in 25 ml. of water. Add 3 ml. of saturated bromine water and heat on steam bath for 15 minutes. Neutralize the solution with conc. HCl. Boil to remove the bromine and filter. Dilute the filtrate to 25-50 ml., transfer to a Nessler tube, and proceed as described under "General".

Procedure - Analysis of Potassium Chloride and Sodium Chloride

Weigh accurately a 10 g. sample into a Nessler tube and dissolve with 30 ml. of water. Proceed as described under "General".

Procedure - Analysis of Hydrofluosilicic Acid

Evaporate a 1 g. sample in a platinum dish on a steam bath with 1 ml. of HF. Moisten the residue with 5 drops of conc. HCl and add 30 ml. of distilled water. Filter, transfer to a Nessler tube, and proceed as described under "General".

Procedure - Analysis of Sodium Dichromate

One gram of sample is dissolved in approximately 30 ml. of distilled water. One ml. of 6 N HCl and 10 ml. of 10% barium chloride solutions are added. The solution is brought to volume in a 100 ml. Nessler tube and compared with a second Nessler tube containing a standard dichromate solution to which 5 ml. of 0.001 g/ml of standard sulfate has been added. The sulfate is reported as greater or less than 0.5%, depending on turbidity.

Procedure - General

Add 1 ml. of 6 N HCl and 5 ml. of 10% barium chloride solution. Dilute to 50 ml. with distilled water and mix well. To a second Nessler tube, add 30 ml. of distilled water, 1 ml. of 6 N HCl, 5 ml. of 10% barium chloride solution, and dilute to 50 ml. with distilled water. To this second tube, add from a buret enough standard sulfate solution to match the turbidity in the sample tube.

Calculations

$$\% \ SO_4 = \frac{(\text{ml. of std.})(\text{g./ml. of std.})(100)}{\text{g. of sample in Nessler tube}}$$

Literature References

1. Rosin, "Reagent Chemicals and Standards," D. Van Nostrand Co., Inc., New York (1939).

2. "Specifications for Analytical Reagents," American Chemical Society (April, 1950).

Written by: D.G. Miller
Revised: Sept., 1953

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Obsolete as of September 1953
Date

Procedure - Analysis of Oxalic Acid

Weigh accurately a 2 g. sample in a platinum dish and dissolve with 20 ml. of water. Add 10 mg. of sodium carbonate and evaporate to dryness on a steam bath. Ignite to decompose the acid and dissolve the residue in 25 ml. of water. Add 3 ml. of saturated bromine water and heat on steam bath for 15 minutes. Neutralize the solution with conc. HCl. Boil to remove the bromine and filter. Dilute the filtrate to 25-50 ml., transfer to a Nessler tube, and proceed as described under "General".

Procedure - Analysis of Potassium Chloride and Sodium Chloride

Weigh accurately a 10 g. sample into a Nessler tube and dissolve with 30 ml. of water. Proceed as described under "General".

Procedure - Analysis of Hydrofluosilicic Acid

Evaporate a 1 g. sample in a platinum dish on a steam bath with 1 ml. of HF. Moisten the residue with 5 drops of conc. HCl and add 30 ml. of distilled water. Filter, transfer to a Nessler tube, and proceed as described under "General".

Procedure - General

Add 1 ml. of 6 N HCl and 5 ml. of 10% barium chloride solution. Dilute to 50 ml. with distilled water and mix well. To a second Nessler tube, add 30 ml. of distilled water, 1 ml. of 6 N HCl, 5 ml. of 10% barium chloride solution, and dilute to 50 ml. with distilled water. To this second tube, add from a buret enough standard sulfate solution to match the turbidity in the sample tube.

Calculations

$$\% \text{ SO}_4 = \frac{(\text{ml. of std.})(\text{g./ml. of std.})(100)}{\text{g. of sample in Nessler tube}}$$

Literature References

1. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., Inc., New York (1939).

2. "Specifications for Analytical Reagents", American Chemical Society, (April, 1950).

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Date: July, 1952

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Calculations

$$\% \ SO_4 = \frac{(\text{ml of std.})\ (\text{g/ml of std.})\ (100)}{\text{g of sample in Nessler tube}}$$

Literature References

Rosin, "Reagent Chemicals and Standards," D. Van Nostrand Co., Inc., New York (1939).

"Specifications for Analytical Reagents,".American Chemical Society (April, 1950).

Written by: D. G. Miller
Revised: July 20, 1954

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DETERMINATION OF SILICON

Perchloric Acid Dehydration Method

Principle

Silicon and its compounds are converted by proper treatment of the sample to silicic acid, which is then dehydrated to impure silica by fuming with perchloric acid. The amount of silica in the impure solid is determined by volatization of the silica with hydrofluoric acid and weighing the impurities.

$$Na_2SiO_3 + 2HCl \longrightarrow H_2SiO_3 \downarrow + 2NaCl$$

$$H_2SiO_3 \xrightarrow{HClO_4} H_2O + SiO_2 \downarrow$$

$$SiO_2 + 4HF \longrightarrow SiF_4 \uparrow + 2H_2O$$

For the interferences consult the literature references.

Procedure - Analysis of Aluminum-Silicon Alloy

Weigh accurately 0.2 to 0.5 g. sample and transfer to a large nickel crucible. Add 12 ml. of 50% sodium hydroxide. Cover the crucible. After the initial intense reaction subsides, evaporate the sample cautiously to a syrupy consistency. Add portions of 30% hydrogen peroxide drop by drop and evaporate until all the material is in solution. Cool crucible and transfer contents quantitatively to a 400 ml. beaker. Proceed from this point as under "General".

Procedure - Analysis of Calcium Metal

Weigh 5 g. into a 100 ml. platinum dish. Add distilled water (30-40 ml.) cautiously, covering dish almost completely to prevent spattering. After dissolution is complete, transfer contents of the crucible to a 400 ml. beaker. Proceed from this point as under "General".

Procedure - Analysis of Magnesium Oxide

Weigh 1 g. of sample into a platinum crucible. Add approximately 6 times as much C.P. sodium carbonate and mix well. Cover curcible and apply heat cautiously (Fisher burner) until mixture melts, increasing the heat during the reaction. Continue until the melt is clear and homogeneous. Remove the crucible from the heat and rotate the crucible so that a thin layer of melt forms on the side of the crucible. When the melt solidifies, drop crucible and lid into 1" of water, contained in a 400 ml. beaker. Add water to cover the crucible and heat gently until material is in solution. Remove crucible and lid, rinsing well, and proceed as under "General".

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Procedure - Analysis of Sodium Silicate

Take 2 g. of sample and add to 20 ml. distilled water in a 400 ml. beaker. Proceed as under "General".

Procedure - Analysis of Aluminum Nitrate Solution

Take 10 ml. sample and add to 400 ml. beaker. Add 10 ml. concentrated sulfuric acid, heat gently, and add formic acid dropwise until NO_2 fumes are all evolved. Proceed as under "General".

Procedure - Analysis of Sulfamic Acid

Take 10 g. sample and dissolve in 20 ml. of water in a 400 ml. beaker. Proceed as under "General".

Procedure - General

Add concentrated hydrochloric acid to the sample until it is strongly acid, if it is not already acid. Add 20 ml. of perchloric acid and evaporate to fumes of perchloric acid. Fume at least 15 min. (Remark 1), cool, add 100 ml. hot, distilled water, stir well, and heat until salts are dissolved. Filter through Whatman #42 filter paper and wash thoroughly with 10% (by volume) sulfuric acid.

Evaporate the filtrate to small volume, add 10 ml. perchloric acid, and evaporate to fumes as above. Filter as above, using the same filter paper. Wash filter well with hot, distilled water to remove free acids (Remark 2).

Dry precipitate and filter in a platinum crucible, burn paper off slowly, and then ignite at 1000°C for 1/2 hr. Cool in desiccator and weigh.

Moisten residue with concentrated sulfuric acid and add 10 ml. concentrated hydrofluoric acid carefully. Evaporate (steam bath) to dryness and repeat hydrofluoric acid treatment. Ignite residue at 1000°C for 1/2 hr., cool in desiccator, and weigh.

Calculations

Grams SiO_2 in sample = weight before HF treatment minus weight of the treatment = W.

$$\% \; SiO_2 = \frac{W}{S} \times 100$$

$$= \frac{W}{V \times Sp.G.}$$

S = g. sample
V = ml. sample
Sp.G = specific gravity

$$\% \; Si = \% \; SiO_2 \times 0.4672$$

$$ppm \; Si = \% \; Si \times 10^4$$

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Remarks

1. The residue must be thoroughly dehydrated to reduce the solubility of SiO_2 in the subsequent filtration and washing.

2. All the perchloric acid must be removed by thorough washing to prevent a violent reaction when the filter paper is dried and ignited.

Literature References

1. Hildebrand and Lundell, "Applied Inorganic Analysis", John Wiley & Sons, Inc., 722 (1929).

2. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand Co., 804 (1939).

3. A.S.T.M., Chemical Methods of Metals, 145 (1946).

Written by: W. N. Carson
Date: July, 1952

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DETERMINATION OF SILICON
Hydrochloric Acid Dehydration Method

Principle

Silicon and its compounds are converted, by the proper treatment of the sample, to silicic acid which is then dehydrated to impure silica by fuming with hydrochloric acid. The amount of silica in the impure solid is determined by volatilization with hydrofluoric acid and weighing the impurities.

Procedure - Analysis of Sodium Silicate

Digest one to two grams of sample with HCl and evaporate to dryness on a steam bath. Repeat the procedure and take up the residue with 10 ml of 50% HCl and 20 ml of water. Digest for 5 to 10 minutes to dissolve the soluble salts, filter through #42 filter paper and wash thoroughly with distilled water. Transfer the filtrate to a platinum dish and evaporate to dryness on a steam bath. Add approximately 20 ml of distilled water filter and wash again, as above. Dry the residue and ignite at 900°C. Cool residue and moisten with 5 drops H_2SO_4. Dry and ignite again at 900°C. Cool, weigh, and record. Moisten with 5 drops H_2SO_4. Add 10 ml HF and evaporate to a small volume. Add 10 more ml of HF and evaporate to dryness. Ignite at 900°C. Cool and weigh.

Calculations

$$\% \ SiO_2 = \frac{\text{Difference in weight} \times 100}{\text{Weight of sample}}$$

Reference

Furman, "Scott's Standard Methods," D. Van Nostrand, 1939, p. 805.

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DETERMINATION OF SULFATE

Turbidimetric Method

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Principle

The turbidity produced by the formation of insoluble $BaSO_4$ upon the addition of $BaCl_2$ to a solution containing the sulfate ion is visually compared with a standard. Pb, Sr, and Ca interfere due to the insolubility of their sulfates. Reagent blanks should be run and results corrected when these blanks are found to be significant.

Solution

Standard sulfate solution, 0.1 mg. sulfate/ml. Weigh accurately 1.8140 g. of potassium sulfate, which has been previously dried at 110°C for 1 hr. into a 1 l. volumetric flask. Dissolve with 100 ml. of water and dilute to the mark. Mix thoroughly before using.

Procedure - Analysis of Aluminum Nitrate Solution

Weigh accurately 5 g. of sample into a beaker. Add 7 ml. of concentrated hydrochloric acid and evaporate to dryness on a steam bath. Repeat evaporation to dryness with 7 ml. of concentrated hydrochloric acid. Dissolve the residue in 50 ml. of hot water and pour into 80 ml. of 2 M ammonium hydroxide. Boil off excess ammonia. Filter and wash precipitate with water until total volume of filtrate and washings is 200 ml. Transfer a 25 ml. aliquot of the solution to a Nessler tube and neutralize with 1 N HCl. Proceed as described under "General".

Procedure - Analysis of Nitric Acid

Weigh accurately a 10 g. sample into an evaporating dish and add 0.1 g. of solid Na_2CO_3. Evaporate to dryness on a steam bath and dissolve the residue with 30 ml. of water. Transfer the solution to a Nessler tube and proceed as described under "General".

Procedure - Analysis of Phosphoric Acid

Weigh accurately a 3 g. sample into a Nessler tube containing 30 ml. of water. Add conc. ammonium hydroxide until the solution is brought to a pH of 3-5. Proceed as described under "General".

Procedure - Analysis of Hydriodic Acid

Weigh accurately a 3 g. sample into an evaporating dish, add 0.1 g. of sodium carbonate, and evaporate to dryness on a steam bath. Dissolve the residue in 30 ml. of distilled water, transfer to a Nessler tube, and proceed as described under "General".

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DETERMINATION OF TIN

Silico-Molybdate Colorimetric Method

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Principle

Stannous chloride reduces silico-molybdate to molybdenum blue, which is measured spectrophotometrically. Nitrates and hydrogen peroxide interfere.

Solutions

Silicate stock solution. Fuse 1 g. of pure silica with 5 g. of sodium carbonate and dissolve in 1 l. of water.

Molybdate stock solution. Dissolve 5.3 g. of ammonium molybdate in 190 ml. of water and 10 ml. of concentrated sulfuric acid.

Silico-molybdate reagent. Dilute 10 ml. of molybdate stock solution to about 800 ml. with water. Add 2.5 ml. of silicate stock solution and dilute to 1 l. with water. Prepare fresh daily. Let stand at least 30 min. before using.

Standard tin solution, 0.04 mg. Sn/ml. Dissolve 0.08 g. of pure tin in 100 ml. of 6 N hydrochloric acid and dilute to 2 l. with 6 N hydrochloric acid.

Procedure - Analysis of Aluminum Nitrate Solution

Weigh 0.4 g. of solution into a beaker, dissolve in a small amount of water, add 2.5 ml. of concentrated sulfuric acid, and heat gently. Add concentrated formic acid dropwise until all brown fumes of nitrogen dioxide are gone. Heat till white fumes appear and fume for 1 hr. Add 15 ml. of water and proceed as described under "General". Maximum permissible limit, 0.005%.

Procedure - Analysis of Hydrogen Peroxide

Weigh 2 g. of sample into a beaker, add 1 ml. of concentrated sulfuric acid, and evaporate to dryness. Add 15 ml. of water and proceed as described under "General". Maximum permissible limit, 10 ppm.

Procedure - Analysis of Sulfamic Acid

Weigh 0.2 g. of sample into a beaker, add 15 ml. of water, and neutralize to the litmus paper endpoint with concentrated ammonium hydroxide. Proceed as described under "General". Maximum permissible limit, 0.01%.

Procedure - General

To the solution of the sample add 1 ml. of concentrated hydrochloric acid and about 0.5 g. (a small scoop) of test lead. Cover, boil for 10 min., and pour immediately into a 25 ml. graduated cylinder containing 5 ml. of the silico-molybdate reagent. Dilute to 25 ml. with water. Let stand 5 min. before measuring on the spectrophotometer.

Perform a standard in the same manner, substituting 500 ul. of standard tin solution for the sample. Read the sample and the blank against a water reference at 700 mu, using the red sensitive phototube and 5 cm. cells. If the optical density of the sample is less than that of the standard, report as less than the maximum permissible limit.

Literature References

1. Ind. and Eng. Chem., Anal. Ed., 16, 269 (1944).

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Written by: H. H. Van Tuyl
Date: July, 1952

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DETERMINATION OF ZIRCONIUM OXIDE

Gravimetric Method

DECLASSIFIED

Principle

Many organic phosphorus acids give precipitates with zirconium, titanium, tin, thorium, and a few other elements. The precipitate formed by phenylarsonic acid $C_6H_5AsO(OH)_2$, is more insoluble than the others. The zirconyl phenylarsonate is readily ignited to the oxide. When zirconium and titanium occur together, the precipitation of titanium can be prevented by oxidizing with H_2O_2.

Solutions

Phenylarsonic acid, 1%. Let freshly prepared solution stand for 30 min., and filter.

Wash solution. Dissolve 0.5 g. of phenylarsonic acid and 1.0 g. of ammonium thiocyanate in 100 ml. of 0.025 N sulfuric acid solution.

Procedure - Analysis of Zirconium Carbonate Gel

Weigh accurately 0.3 g. of sample and dissolve in 60 ml. of concentrated sulfuric acid. Dilute with about 140 ml. of water and add 3 ml. of 30% hydrogen peroxide and 10 ml. of 1% ammonium thiocyanate. Boil in a hood for 3 min., and then add 100 ml. of 1% phenylarsonic acid slowly and with stirring. Digest until the precipitate coagulates and settles. Cool to room temperature and filter through an ignited and tared Selas filtering crucible, washing the precipitate with the wash solution. Wash precipitate several times with 2% ammonium nitrate solution.

Dry the crucible at 105°-110° in an oven for 1-2 hrs., then place on the edge of the muffle with the door open until the carbon is all burned off. Continue ignition at 900-950°C to constant weight. Cool to room temperature and weigh.

Calculations

$$\% \ ZrO_2 = \frac{(A - B) \times 100}{C}$$

A = g. crucible plus residue
B = g. crucible
C = g. sample

Remarks

1. Condition of sample is important. It should be a thick paste. If watery or hard, a resample should be requested.

2. Zirconium compounds should be sampled and analyzed as soon as received since, after exposure to air, they form compounds of indefinite composition.

July, 1952

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Code Zr-1

References

1. Rice, Fogg, and James, J.A.C.S., 48, 895 (1926).

2. G. C. Chandlee, J.A.C.S., 57, 8 (1935).

3. Simpson and Chandlee, Ind. Eng. Chem., Anal. Ed. 10, 642 (1938).

4. Furman, "Scott's Standard Methods of Chemical Analysis", D. Van Nostrand Co., 1102 (1938).

DECLASSIFIED

Written by: W. G. Burch
Date: July, 1952

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[redacted]

DETERMINATION OF ORGANIC MATTER

Extraction Method

Principle

A measured volume of the sample is diluted with water and the solution extracted with diethyl ether. The ether extract is evaporated to dryness and the residue weighed.

Procedure - Analysis of Sulfuric Acid

Add 50 ml. of the acid to 200 ml. of water and transfer the solution, when cool, to a 500 ml. separatory funnel. Extract twice with 100 ml. of A.C.S. grade, diethyl ether and a third time with 50 ml. Combine the ether extracts and wash with three 100 ml. portions of water, combining the aqueous portions. Extract these with 50 ml. of ether.

Transfer the ether extracts to a tared dish or flask and evaporate to dryness on a steam bath. Dry the residue in a current of purified air and weigh.

Calculations

$$\% \text{ organic matter} = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

Remarks

1. All operations in this determination should be performed in a well ventilated hood and with careful control of flames or electric sparks in the room.

Written by: W. W. Mills
Date: July, 1952

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OXALIC ACID DETERMINATION

Volumetric Method

Principle

Oxalic acid, like many unsaturated organic compounds, acts as a reducing agent for strong oxidizing agents. The reaction is stoichiometric and can be used for the quantitative determination of the compound. The presence of other reducing agents interferes.

$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Solutions

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Standardized potassium permanganate, 0.1 N.

Procedure

Weigh accurately 3 g. of sample into a 500 ml. volumetric flask containing about 100 ml. of water. Dissolve the solid completely and dilute to the mark. Mix the solution and pipet a 10 ml. aliquot to an Erlenmeyer flask. Add 3 ml. each of concentrated sulfuric and phosphoric acids. Dilute the solution with 25 ml. of water. Add from a buret 8 ml. of standardized potassium permanganate. Heat the solution to 90°C and complete the titration of the hot solution to the endpoint, which is indicated by a pink coloration that is stable for about one min.

Calculations

$$\% \ (COOH)_2 \cdot 2H_2O = \frac{(\text{ml. } KMnO_4)(\text{normality})(.06303)(100)}{\text{g. of sample in aliquot}}$$

Literature References

1. Furman, "Scott's Standard Methods of Chemical Analysis," II, 5th Ed., D. Van Nostrand Co. (1939).

2. Rosen, "Reagents, Chemicals, and Standards", D. Van Nostrand Co. (1937).

Written by: R. E. Ewing
Date: July, 1952

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Code Zx-5

DETERMINATION OF BUTANOL

Volumetric Method

Principle

Alcohols are oxidized by dichromate in acid solution. Since the reaction is slow, an excess of standard dichromate is added, the sample is heated, and the excess is then determined by titration with standard ferrous ammonium sulfate. Any reducing substance will be reported as butanol.

Solutions

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Standardized potassium dichromate, 0.1 N.

Standardized ferrous ammonium sulfate, 0.1 N.

Ferroin indicator, 0.025 M.

Procedure - Analysis of Tributylphosphate

Pipet 10 ml. of the sample into an Erlenmeyer flask, add 10 ml. of 6 N sulfuric acid and 0.1 N standard potassium dichromate solution until a stable yellow color appears. Heat on the hot plate, with mixing, for 3 min. Cool under running water. Add one drop of ferroin indicator and titrate with standard ferrous ammonium sulfate to the first permanent orange color.

Calculations

$$\text{Reducing normality} = \frac{(V_D \times N_D) - V_F \times N_F}{\text{ml. sample}}$$

V_D = ml. of potassium dichromate
N_D = normality of potassium dichromate
V_F = ml. of ferrous ammonium sulfate
N_F = normality of ferrous ammonium sulfate.

Written by: G. B. Barton
Date: July, 1952

[redacted] DECLASSIFIED ~~RESTRICTED~~

DETERMINATION OF MESITYL OXIDE

Spectrophotometric Method

Principle

The mesityl oxide concentration is determined spectrochemically at a wave length of 231 millimicrons against pure iso-octane as a blank. It is necessary to obtain a spectrochemical factor from known amounts of pure mesityl oxide. This factor must be redetermined when a new batch of solvent is used, or if the mesityl oxide is redistilled.

Hexone in concentrations greater than 2 ug. per ml. will give high results for which a correction must be applied. The accuracy of the method is dependent upon the purity of the mesityl oxide used as a standard, the care with which dilutions are made, and the proper use of the Beckman quartz spectrophotometer.

Solutions

Iso-octane, highest purity.

Hexone, Shell purified.

Mesityl oxide, freshly distilled. Add 35 ml. of mesityl oxide into a 50 ml. distilling flask with 4 or 5 bumping stones. Use a water condenser to condense the vapor and a glass-col mantle to heat the sample.

Collect approximately 2 ml. of distillate in a 10 ml. graduated cylinder, using this to rinse the graduate. Discard this rinse and continue to collect the distillate at the rate of 10 drops per minute until the temperature reaches 130°C or until the flask is practically dry.

Store in a glass stoppered Pyrex bottle. The boiling point of mesityl oxide is 128-130°C.

Procedure - Analysis of Hexone

Pipet three 50 ul. portions of the sample (Remark 1) into separate 10 ml. volumetric flasks. Rinse the pipet three times with iso-octane, adding the rinsings to the flask. Pipet 25 ul. of mesityl oxide stock solution into one of the flasks as a spike. Dilute to mark with iso-octane and shake well.

Pipet 50 ul. (or size of sample) of Shell purified hexone into another 10 ml. volumetric flask. Dilute to mark with iso-octane.

Read the optical densities of the samples, spike, and hexone dilution against pure iso-octane at 231 mu and a slid width of 0.9 mm. in 1 cm. silica cells.

To calibrate the instrument, prepare a stock solution consisting of 50 ul. of mesityl oxide (Remark 2), diluted to 50 ml. with iso-octane. Pipet 25, 50, 75, and 100 ul. of stock solution into separate 10 ml. volumetric flasks. Rinse the pipet three times with iso-octane, adding the rinsings to the flask. Dilute to mark with iso-octane. Mix well by shaking.

Read the optical density of the solutions against pure iso-octane at 231 mu with a slit width of 0.9 mm. in 1 cm. silica cells.

Determine the spectrochemical factor for the mesityl oxide stock solution by averaging the individual factors found for each dilution.

$$\text{Factor} = \frac{V \times 10^{-6}}{W}$$

V = ul. of mesityl oxide stock solution
W = optical density.

Calculations

$$\% \text{ by volume mesityl oxide} = \frac{(A-B)C \times 100}{D}$$

A = average optical density of duplicate samples
B = optical density of hexone dilution
C = spectrochemical factor
D = ml. of sample.

$$\% \text{ recovery} = \frac{(E-A)C \times 100}{F}$$

E = optical density of spike
F = ml. of mesityl oxide in spike.

Remarks

1. The sample should contain 0.03-0.10 ul. of mesityl oxide. This will normally be contained in 50 ul. of hexone.

2. Mesityl oxide is hygroscopic and must be redistilled once every month.

References

1. Barton, G. B., Hanford Works Secret Notebook, HW-2469-T.

2. Knott, D. M., Hanford Works Secret Notebook, HW-2197-T.

3. Temple, M. K., Hanford Works Secret Notebook, HW-2715-T.

Written by: D. W. Brite
Date: July, 1952

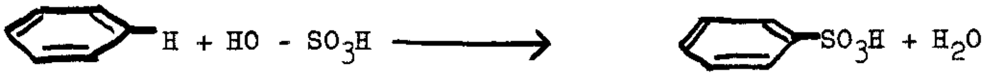
DETERMINATION OF AROMATIC HYDROCARBONS

Semi-Quantitative Method

DECLASSIFIED

Principle

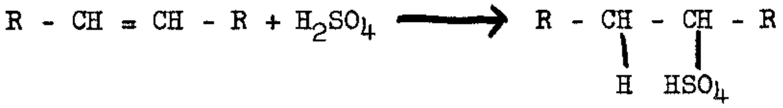
Aromatic hydrocarbon compounds, when contacted with anhydrous sulfuric acid, are converted to sulfonates. The sulfonates are soluble in the sulfuric acid phase.



Phosphorus pentoxide may be employed to insure that the sulfuric acid remains anhydrous.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

Olefinic hydrocarbons, if present in the sample, also react with sulfuric acid.



$$R - CH = CH - R + H_2SO_4 \longrightarrow R - \underset{H}{CH} - \underset{HSO_4}{CH} - R$$

The resulting alkylsulfuric acid, like the sulfonates, is soluble in the sulfuric acid phase. An independent olefin determination must therefore be performed and a correction for olefins must be applied.

Solutions

Sulfuric acid-phosphorus pentoxide mixture, 70% sulfuric acid-30% phosphorus pentoxide. Add 275 g. of phosphorus pentoxide to 350 ml. of concentrated sulfuric acid in an 800 ml. beaker. Stir until the phosphorus pentoxide is dissolved. Pour the solution into a 500 ml. glass-stoppered ether bottle with a glass cap to keep moisture from collecting on the lip of the bottle.

Procedure - Analysis of Petroleum Diluent

Add 25 ml. of the sulfuric acid-phosphorus pentoxide reagent to a sulfonation flask, stopper the flask, and place in an ice bath in a hood for 5 min.

Record the temperature of the sample. Pipet 10 ml. into the flask, allowing the sample to run down the sides of the flask so that mixing of the two layers does not occur. (Remark 1) Place the flask in the ice bath for another 5 min.

Shake the flask cautiously (Remark 2) in the ice bath for 2 min., so that the layers mix. Raise the flask above the ice bath and shake for 20 sec. with a vertical wrist motion at a rate of 150-200 3 to 4-inch strokes per min. Replace immediately in the ice bath and shake for 40 sec. Continue shaking the flask alternately out of the bath 20 sec. and in 40 sec., until a total shaking time of 10 min. has elapsed.

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Remove the flask from the ice bath and vent the flask momentarily. Centrifuge for 3 min. at 1000 rpm. Pour concentrated sulfuric acid down the side of the flask until the hydrocarbon layer is entirely within the calibrated portion of the flask. Centrifuge for 3 min. more.

Adjust the temperature of the sample to within 1°C of the temperature at which the sample was measured. Determine the volume of the unreacted portion of the sample.

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Calculations

% by volume aromatics = 100 - 10R - C - U

R = ml. of unreacted sample
C = correction for solubility of the unreacted portion in the acid layer, which is taken as 1
U = % olefins as found in olefin determination.

Remarks

1. There is a large initial heat of reaction for samples rich in olefins. For such samples it is desirable to vent the small amount of pressure which builds up with the first shaking.

2. A face mask should be worn by the analyst from this point on.

References

1. A.S.T.M. Standards 1949, Part 5, pp. 1040-1044 (D875-46T).

Written by: D. W. Brite
Date: July, 1952

DECLASSIFIED

DETERMINATION OF OIL AND GREASE

Gravimetric Method

Principle

The oil and grease are extracted into carbon tetrachloride and recovered from the solvent by evaporation.

Procedure - Analysis of Calcium

Accurately weigh a 50 g. sample into the alundum thimble of a medium Soxhlet extractor. Assemble the extractor with 125 ml. of carbon tetrachloride (Remark 1) and reflux for 1 hr.

Remove the flask containing the solvent and distill off all but 15 ml. of the solvent (Remark 2). Filter the remaining solution through dry #1 filter paper into a tared glass dish and wash once.

Evaporate the sample to dryness with a filtered air stream, dry in a desiccator, and weigh the residue.

Calculations

$$\% \text{ grease and oil} = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

Remarks

1. All apparatus should be dried in an oven before use.
2. The distilled solvent may be recovered and used again.

Written by: A. Chetham-Strode
Date: July, 1952

[redacted] DECLASSIFIED [redacted]

DETERMINATION OF OLEFINIC HYDROCARBONS

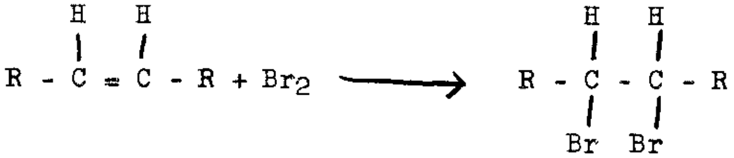
Volumetric Method

DECLASSIFIED

Principle

Olefinic hydrocarbons enter into an addition reaction with free bromine. If an excess amount of bromine is present, the excess can be determined by the addition of iodide and the titration of the resulting iodine with thiosulfate. The bromine number of the sample (grams of bromine that react with 100 grams of the sample) is determined in this manner. The olefin concentration may be calculated from the bromine number if the average molecular weight of the olefins is known (Remark 1).

$$6HAc + KBrO_3 + 5KBr \longrightarrow 6KAc + 3Br_2 + 3H_2O$$



$$R-CH=CH-R + Br_2 \longrightarrow R-CHBr-CHBr-R$$

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Solutions

Potassium bromide-bromate solution, 0.5 N. Dissolve 49.6 g. of potassium bromide and 13.9 g. of potassium bromate in distilled water and dilute to 1 liter. Pipet exactly 5 ml. of this solution, drop by drop, at a rate of 1-2 drops per second, while the flask is shaken with a swirling motion, into 50 ml. of acetic acid and 5 ml. of carbon tetrachloride in a 500 ml. iodine-number flask. Shake the solution well and allow to stand 5 minutes.

Proceed as in paragraph 3 of the procedure for determining olefins.

$$\text{Normality of bromide-bromate} = \frac{V_1 N_1}{5}$$

V_1 = ml. of thiosulfate
N_1 = normality of thiosulfate.

Standardized sodium thiosulfate solution, 0.1 N.

Procedure - Analysis of Petroleum Diluent

Weigh or pipet 3-5 g. of the sample into a volumetric flask and dilute to exactly 50 ml. with carbon tetrachloride. Pipet immediately a 5 ml. aliquot into a 500 ml. iodine-number flask containing 50 ml. of glacial acetic acid.

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July, 1952

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Titrate with the bromide-bromate reagent at the rate of 1-2 drops per second while swirling the contents of the flask until a distinct yellow color persists for 5 seconds. Do not expose the flask to direct sunlight. Add an additional 1 ml. of reagent, stopper the flask and continue shaking for 40 seconds. Record the volume of reagent used.

Add immediately 5 ml. of potassium iodide solution (150 g. per 1.), by placing in the lip of the flask and removing the stopper momentarily. Shake vigorously, add 100 ml. of water, and shake vigorously again for 1 min. Titrate with 0.1 N sodium thiosulfate. When the solution becomes light in color, add 1 ml. of starch solution (5 g. per 1.) and continue the titration to a colorless endpoint.

Calculations

$$\text{Bromine number} = \frac{V_b N_b - V_t N_t}{A} \times 7.992$$

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V_b = ml. of bromide-bromate
N_b = normality of bromide-bromate
V_t = ml. of thiosulfate
N_t = normality of thiosulfate
A = g. of sample in aliquot.

$$\%\ \text{olefins by volume} = \frac{B \times M}{160}$$

B = bromine number
M = molecular weight of olefins.

Remarks

1. Relation of olefin molecular weight to A.S.T.M. 50% boiling point.

A.S.T.M. 50% Boiling Point	Molecular Weight of Olefin
300°F	127
350°F	145
400°F	164
450°F	185
500°F	208

References

1. A.S.T.M. Standards 1949, Part 5, pp. 1037-1040 (D875-46T).

Written by: D. W. Brite
Date: July, 1952

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DETERMINATION OF APPEARANCE

DECLASSIFIED

Principle

The samples are inspected visually and their appearance noted.

Procedure - Analysis of Bromobenzene

Compare sample with distilled water. It should be water clear to pass the test.

Procedure - Analysis of Carbon Tetrachloride

Inspect the sample visually. It should be clear, colorless, and free of suspended matter.

Procedure - Analysis of Methanol

Compare 25 ml. of sample in a Nessler tube with an equal volume of distilled water in another Nessler tube. Color and clarity of the two solutions should match.

Procedure - Analysis of Sulfuric Acid

Inspect the sample for color. It must in no case be darker than a clear light amber.

Written by: R. Ko
Date: July, 1952

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DISTILLATION RANGE

Distillation Method

DECLASSIFIED

Principle

Organic substances, particularly those which are liquids at room temperature, have a definite boiling point at a specified pressure. The distillation range is defined as the difference between the temperature at which distillation begins and the temperature at which all of the material has been distilled. The distillation range is used as a means of determining the variation around the true boiling point of the substance.

Procedure - Analysis of Bromobenzene, Carbon Tetrachloride, Methanol, Methyl Isobutyl Ketone, Trichloroethylene.

Measure 100 ml. of the sample into the flask of a clean distillation apparatus. Assemble the apparatus. Heat the distillation flask rapidly until the material begins to boil. Reduce the rate of heating so that the condensate is received at the rate of 1-2 drops per second.

Read the temperature at which the first drop of condensate is received. Continue the distillation until all the material has distilled. Read the temperature at which the bottom of the flask goes to dryness, or at which smoke or very heavy vapors suddenly appear. Discontinue heating.

Calculations

Distillation range = Final temperature - Initial temperature.

Literature References

1. A.S.T.M. Standards, Part III, Designation D86-40, 131-136 (1942).

Written by: R. E. Ewing
Date: July, 1952

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DETERMINATION OF MELTING POINT

Physical Method

Principle

A sample is placed in a capillary tube and slowly heated. The temperature at which the sample melts is recorded as the melting point of the material.

Procedure - Analysis of Acenaphthene

Powder about 5 g. of material and fill a capillary tube to form a column of 2.5-3.5 mm. of packed material. Attach the capillary to a thermometer, keeping the material beside the thermometer bulb. Immerse in a mineral oil bath, holding the thermometer bulb about 2 cm. from the bottom of the bath.

Heat the oil bath in a hood and agitate the oil continuously. At 30°C below supposed melting point, regulate heat so that temperature rises approximately 3°C per minute. Record the temperature when sample first appears to melt and reduce heating rate so that temperature rises about 0.5°C per minute.

Record the temperature at which the last trace of solid melts. The average temperature is recorded as the melting point of the material. Duplicate analyses should be made and check within 0.5°C.

Literature References

1. "The United States Pharmacopoeia", 12th Rev., Mack Printing Co., Easton, Pa., 595 (November, 1942).

Written by: R. I. Miller
Date: July, 1952

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DETERMINATION OF REFRACTIVE INDEX

Physical Method

DECLASSIFIED

Principle

All liquids have a characteristic refractive index value which can serve as a purity criterion. These values are by no means unique since other liquids or mixtures of liquids may yield the characteristic value of the pure substance.

Apparatus

Refractometer

Procedure - Analysis of Hexone

Read the operating instructions which pertain to the instrument and measure the refractive index of a suitable sample. Report the refractive index as the value obtained for a sample at 20°C and with reference to sodium light (589 mu). Estimate the value to the fourth decimal place.

Written by: T. K. Bierlein
Date: July, 1952

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FLASH POINT OF PETROLEUM DILUENT

Closed Cup Method

DECLASSIFIED

Principle

The temperature of the oil under test is gradually raised until a flash of light is detected with the test flame. In the closed cup method, the oil vapor is confined within the enclosed walls of the tester. In the open cup method, as the name implies, the tester is open and the oil vapor is not confined but escapes freely into the atmosphere.

Apparatus

Tag closed tester.

Two A.S.T.M. P.M. and Tag thermometers, +20° to +230°F.

Procedure - Analysis of Petroleum Diluent

Place oil cup in proper position and measure 50 ml. of sample into it. Temperature of sample and of water bath must be at least 20°F below probable flash point when test is started.

Destroy air bubbles on surface of sample and attach cover with flash point thermometer to bath collar.

Light test flame and adjust it to size of white bead on cover. Light gas burner and place it centrally in base of tester. Adjust flame so that temperature of sample rises approximately 1.8°F per min., not faster than 2°F nor slower than 1.6°F per min. Record barometric pressure and initial temperature of sample.

When temperature of sample is 9°F below its probable flash point, turn knob on cover to introduce test flame into vapor space of cup and immediately turn back again. About 1 full second is consumed in turning knob down and back.

Record time and temperature of sample at first introduction of test flame. Repeat application of test flame after each 1°F rise in temperature of sample until distinct flash is observed.

Do not confuse flash with bluish halo sometimes surrounding test flame during applications immediately preceding actual flash. Record time and temperature of sample when flash point is reached. If test is to be repeated, use fresh sample. When barometric pressure is below 760 mm., add 1.6°F for each 25 mm. of barometer difference; when above 760 mm., deduct 1.6°F for each 25 mm.

References

1. A.S.T.M. Standards, 1949, Part 5 (D56-36), pp. 687-690.

Written by: R. Ko
Date: July, 1952

DECLASSIFIED

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DETERMINATION OF ODOR

Qualitative Method

DECLASSIFIED

Principle

Methyl alcohol has a characteristic odor, free from pyrogenic, acetic or acetone like odors.

Procedure - Analysis of Methanol

Compare the odor of the sample with that of pure methanol at the same temperature by saturating filter paper with the material and observing the odor. The sample should have an odor characteristic of pure methanol; free from pyrogenic, acetic or acetone like odors and should not have a residue odor upon evaporation.

Written by: D. W. Brite
Date: July, 1952

DECLASSIFIED

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DETERMINATION OF VISCOSITY

Kinematic Method

DECLASSIFIED

Principle

Viscosities of petroleum diluents are measured in terms of the number of seconds required for a specified volume of diluent to flow, at a given temperature, through a capillary tube of specified length and diameter. Kinematic viscosity in centistokes is obtained by multiplying the efflux time by the viscosimeter constant.

The Series 50 modified Ostwald viscosimeter is limited to the range of 300-1500 sec. efflux time or of 0.8-3 centistokes.

Apparatus

Modified Ostwald viscosimeter, Series 50.

A.S.T.M. kinematic viscosity test thermometer, range 74.5-79.5°F.

Procedure - Analysis of Petroleum Diluents

Clean the viscosimeter by rinsing twice with petroleum ether and remove the ether by suction. If the sample is not clean, filter more than 10 ml. through a medium sintered glass filter or a 100 mesh screen.

Introduce 10 ml. of the sample into the viscosimeter through the arm with the larger bore. Immerse the viscosimeter in a water bath regulated at 77°F (25°C), so that the upper bulb is below the surface of the water. Adjust to a vertical position and allow at least five minutes for the sample to attain bath temperature.

Apply suction to the capillary arm to draw the sample up to a point about 5 mm. above the mark between the bulbs. Release the suction and measure the time in seconds required for the meniscus to pass from the upper to the lower mark.

Run a check determination by again drawing the sample above the etched line between the bulbs and timing as before.

Calculations

Viscosity in centipoises = t x c x sp. gr.

t = efflux time in seconds
c = viscosimeter constant (Remark 1)
sp.gr. = specific gravity of sample.

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Remarks

1. The viscosimeter constant is determined by the above procedure, using the efflux times for distilled water at 77°F. The kinematic viscosity of water shall be taken as 0.894 centistokes at 77°F.

$$\text{Viscosimeter constant} = \frac{0.894}{\text{Efflux time in seconds}}$$

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References

1. A.S.T.M. Standards 1949 (D445-46T), Part 5, pp. 906-909.

Written by: M. C. Lambert
Date: July, 1952

DETERMINATION OF SPECIFIC GRAVITY

Pycnometer Method

DECLASSIFIED

Principle

The specific gravity of a substance may be determined by weighing the substance at a specified temperature and dividing this weight by the weight of an equal volume of water at a specified temperature. For example, a specific gravity, 0.952 at 25°C/4°C, of a substance means that the ratio of its weight at 25°C to the weight of an equal volume of water at 4°C is 0.952.

Procedure - Analysis of Bromobenzene and Tributylphosphate

Adjust the temperature of the water bath to 20°C and proceed according to the general procedure.

Procedure - Analysis of Methanol

Adjust the temperature of the water bath to 15°C and proceed according to the general procedure.

Procedure - Analysis of Petroleum Diluent

Adjust the temperature of the water bath to 25°C and proceed according to the general procedure.

Procedure - General

Weigh a clean, dry Reischauer pycnometer to four decimal places. Fill the pycnometer with a slight excess of boiled distilled water and bring it to constant temperature by immersion in the water bath for 15 min. At the end of this time remove the excess water with a glass capillary tube, wipe the pycnometer dry, and weigh to four decimal places.

Using the same pycnometer, repeat the appropriate steps of the above procedure for the substance being analyzed.

Calculations

$$\text{Sp.Gr. at } T_x/T_w = \frac{W_x - W_p}{W_w - W_p} \cdot \frac{D_x}{D_w}$$

W_p = wt. of empty pycnometer
W_x = wt. of pycnometer full of substance x
W_w = wt. of pycnometer full of water
D_x = density of water at T_x degrees
D_w = density of water at T_w degrees.

July, 1952

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Material Analyzed	Temperature Specification T_x/T_w
Bromobenzene	20°C/4°C
Methanol	15°C/4°C
Tributylphosphate	20°C/20°C
Petroleum diluent	25°C/4°C

DECLASSIFIED

References

1. "Handbook of Chemistry and Physics", 31st ed., Chemical Rubber Publishing Co., Cleveland, Ohio, p. 1720 (1949).

2. "Physico-chemical Methods", Vol. I, 4th ed., J. Reilly and W. N. Rae, D Van Nostrand Co., Inc., New York, p. 491 (1943).

Written by: J. A. Parodi
Date: July, 1952

DECLASSIFIED [redacted]

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DETERMINATION OF SOLUBILITY

Qualitative Method

DECLASSIFIED

Principle

The sample is treated with an excess of chloroform, in which it is soluble, and examined for completeness of solution.

Procedure - Analysis of Acenapthene-A-

Weigh 33.0 g. of acenapthene and place in a clean, dry 100 ml. Nessler tube. Add 67.0 ml. of chloroform and cool to 20°C. Close the tube with a tin-foil covered stopper and shake to dissolve solids. At this temperature the sample should be completely soluble and the resultant solution colorless and free of suspended matter.

Literature References

1. 300 Area - Essential Materials Acceptance Specifications.

Remarks

1. Acenapthene-A- is soluble to the extent of 76 g. per 100 ml. of chloroform at 20°C.

Written by: M. W. Gift
Date: July, 1952

DECLASSIFIED

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DETERMINATION OF ETHER EXTRACTABLES

Gravimetric Method

DECLASSIFIED

Principle

Many substances, especially organic materials, are much more soluble in ether than in nitric acid, and therefore, can be extracted from nitric acid with ether.

Procedure - Analysis of Nitric Acid

Pipet 10 ml. of nitric acid, previously cooled in an ice bath, into a separatory funnel and shake with three successive 10 ml. portions of absolute ether.

Combine the ether fractions and wash with three 10 ml. portions of distilled water. Transfer the ether fraction to a tared evaporating dish and evaporate to dryness on a steam bath.

A current of filtered air will help to speed the evaporation, especially near the end when relatively non-volatile constituents remain. Weigh the residue.

Calculations

$$\%\ \text{ether extractables} = \frac{\text{g. residue} \times 100}{\text{ml. sample} \times \text{sp.gr. sample}}$$

Written by: J. A. Parodi
Date: July, 1952

DECLASSIFIED

Code Zy-14

WATER INSOLUBLES DETERMINATION

Gravimetric Method

DECLASSIFIED

Principle

All material not dissolved by water is classified as water insoluble material.

Procedure - Analysis of Aluminum Nitrate Solution

Weigh 15 g. of solution into beaker. Dilute with 100 ml. of hot water and proceed as described under "General".

Procedure - Analysis of Potassium Permangate

Weigh 10 g. of sample into a clean beaker and dissolve in 100 ml. of hot water free of all reducing materials. Proceed as described under "General", using a coarse sintered glass crucible instead of the Gooch crucible.

Procedure - Analysis of Ferrous Ammonium Sulfate

Weigh 10 g. of sample into a beaker and dissolve with 0.5 ml. of concentrated sulfuric acid, diluted to 100 ml. with water. Proceed as described under "General".

Procedure - Analysis of Ammonium Sulfate, Ammonium Fluosilicate, Ammonium Sulfite, Barium Chloride, Calcium Chloride, Lanthanum Ammonium Nitrate, Metso, Naccanol, Oxalic Acid, Potassium Hydroxide, Potassium Chloride, Sodium Carbonate, Sodium Nitrate, Sodium Chloride, Sodium Sulfite, Sodium Pyrophosphate, Sodium Nitrite

Weigh 10 g. of sample into a beaker and dissolve with 100 ml. of hot water. Proceed as described under "General".

Procedure - General

Digest the solution of the sample on the steam bath for 1 hr. Filter the hot solution through a tared Gooch crucible. Wash the beaker and residue with six 10 ml. portions of hot water.

Dry crucible and contents to constant weight at 105°C.

Calculations

$$\% \text{ insoluble} = \frac{(\text{g. insoluble})(100)}{\text{g. sample}}$$

Literature References

1. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., (1934).

Written by: R. E. Ewing
Date: July, 1952

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Code Zy-15

DETERMINATION OF SUSPENDED SOLIDS

Gravimetric Method

DECLASSIFIED

Principle

Extraction of tributyl phosphate with kerosene removes the kerosene soluble suspended solids. Weighing the precipitate remaining after filtration permits calculation of the kerosene insoluble suspended solids originally present.

Procedure - Analysis of Tributyl Phosphate

Weigh 100 ml. of tributyl phosphate into a 250 ml. stoppered graduate and add 100 ml. kerosene. Extract by inverting the graduate 25 times. Filter through a fine, tared, sintered glass crucible, using vacuum. Wash several times with kerosene and dry in oven at 110°C. Cool in desiccator and weigh.

Calculations

$$\% \text{ Solids} = \frac{\text{g. of solids} \times 100}{\text{g. of sample}}$$

Written by: C. E. Michelson
Date: July, 1952

DECLASSIFIED

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[redacted]

DETERMINATION OF NITRIC ACID INSOLUBLE

Gravimetric Method

DECLASSIFIED

Principle

A weighed sample is dissolved in nitric acid of appropriate strength and digested for a suitable period of time. The residue is filtered, dried, weighed, and the results calculated as percent of the original sample. Residues from samples containing bismuth salts are washed with nitric acid to avoid formation of insoluble, basic bismuth salts which would give high results.

Extreme care must be taken to obtain reliable results, especially in cases where the amount of insoluble material is low.

Procedure - Analysis of Bismuth

Weigh accurately 5 g. of sample and dissolve with 60 ml. of concentrated nitric acid. Boil for a few minutes to insure complete dissolution of all soluble material. Dilute the sample with 100 ml. of 10% nitric acid and filter through a tared crucible. Wash the precipitate with six 10 ml. portions of 10% nitric acid, dry at 110°, and weigh.

Procedure - Analysis of Bismuth Subnitrate

Weigh accurately a 10 g. sample and dissolve in 100 ml. of 3 N nitric acid. Digest for 10 min. at 60°C, using a steam bath. Filter through a tared crucible, wash with six 10 ml. portions of 10% nitric acid, dry at 110°C, and weigh.

Procedure - Analysis of Ceric Ammonium Nitrate and Zirconyl Gel

Weigh accurately a 10 g. sample, dissolve in 100 ml. of 3 N nitric acid, digest at 70°C for 10 min., and filter through a tared crucible. Wash the residue with six 10 ml. portions of hot water, dry at 110°C, and weigh.

Procedure - Analysis of Sodium Bismuthate

Dissolve a 10 g. sample by the addition of 25 ml. of distilled water, followed by 25 ml. of 70% nitric acid and 10 ml. of 30% hydrogen peroxide. Heat nearly to boiling for 10 min., filter through a tared crucible, wash with six 10 ml. portions of 10% nitric acid, dry at 110°C, and weigh.

Calculations

$$\% \text{ Insoluble} = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

References

1. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., (1939).

Written by: H. R. Schmidt
Date: July, 1952

DECLASSIFIED

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DETERMINATION OF SUBSTANCES NOT PRECIPITATED BY HYDROCHLORIC ACID

Gravimetric Method

DECLASSIFIED

Principle

Silver chloride is precipitated from an aqueous solution by adding hydrochloric acid. Total solids remaining in solution are classified as substances not precipitated by hydrochloric acid.

Procedure - Analysis of Silver Nitrate

Weigh 25 g. of sample into a 600 ml. beaker, add 350 ml. of water, and heat to boiling. Slowly add 15 ml. of concentrated hydrochloric acid, dilute to about 400 ml., and let stand overnight. Filter and dilute filtrate to exactly 500 ml.

Evaporate a 100 ml. aliquot to dryness. Heat the residue with 10 ml. of water containing 2 drops of hydrochloric acid, and filter. Wash with 10 ml. of water, and dry the filtrate to constant weight in a tared evaporating dish.

Perform a blank, using the same procedure, without addition of the sample.

Calculations

$$\% A = \frac{(B-C) \times 500}{D}$$

where A = substances not precipitated by hydrochloric acid
B = g. of residue from sample
C = g. of residue from blank
D = g. of initial sample

Literature References

1. American Chemical Society, "Specifications for Analytical Reagents", p. 101 (1941).

2. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., p. 365 (1934).

Written by: H. H. Van Tuyl
Date: July, 1952

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DETERMINATION OF OXIDIZING IMPURITIES

Spectrophotometric Method

DECLASSIFIED

Principle

Oxidizing impurities in hexone react with ferrous ammonium sulfate to form ferric iron, which is determined with the spectrophotometer after formation of the thiocyanate complex of ferric ion. The iron must be kept in the ferrous state prior to addition of the sample and is made up in sulfamic acid for this purpose. The SCN^- concentration must be high to minimize errors resulting from the formation of colorless ferric complexes with chloride, phosphate, sulfate, and other ions in acid solution. Several metal ions also form colored complexes with thiocyanate and will interfere. The concentration of these interferences is reduced by a preliminary water wash.

Solutions

Standard ferric solution, 0.1 N. Dissolve 39.214 of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in 100 ml. 1 N HNO_3, heat to boiling, cool, and make up to 1 liter with distilled water in a volumetric flask.

Dilute standard ferric solution, 0.001 N. Dilute 1 ml. of 0.1 N ferric solution to exactly 100 ml.

Dilute standard ferric solution, 0.005 N. Dilute 5 ml. of 0.1 N ferric solution to exactly 100 ml.

Dilute standard ferric solution, 0.010 N. Dilute 10 ml. of 0.1 N ferric solution to exactly 100 ml.

Dilute standard ferric solution, 0.015 N. Dilute 15 ml. of 0.1 N ferric solution to exactly 100 ml.

Standardized ferrous ammonium sulfate, 0.05 N. Make up 19 ml. concentrated HNO_3 + 0.9709 g. NH_2SO_3H + 19.6075 g. $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ to 1 liter with distilled water.

Sodium thiocyanate, 10 g. per liter. Make up 25 ml. concentrated H_2SO_4 + 10 g. NaSCN to 1 liter with distilled water.

Procedure - Analysis of Hexone

Dilute 1 ml. of each of the dilute standard ferric solutions to 100 ml. with the sodium thiocyanate solution and read in the spectrophotometer in 1 cm. cells at 475 mu against a NaSCN blank. Plot a calibration curve showing per cent transmittance against normality of the dilute standard ferric solutions added.

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Shake 10 ml. of the sample with 0.5 ml. of distilled water and discard the aqueous phase. Add 2 ml. of the ferrous ammonium sulfate solution and shake for 1 hr. Dilute 1 ml. of the aqueous phase to 100 ml. with the sodium thiocyanate solution and read immediately in the spectrophotometer in 1 cm. cells at 475 mu against a NaSCN blank.

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Calculations

$$\text{oxidizing normality} = \frac{\text{normality from calibration curve}}{5}$$

Literature References

1. Marsden, J. to Greager, O. H., GE-N-12983 (6/15/48).

Written by: A. Chetham-Strode
Date: July, 1952

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DETERMINATION OF REDUCING IMPURITIES

Permanganate Method

DECLASSIFIED

Principle

A known volume of acid is heated with a specific amount of potassium permanganate as a limit test for reducing impurities.

Solutions

Potassium permanganate, 0.1 N.

Procedure - Analysis of Phosphoric Acid

Add 5 ml. of distilled water and 0.2 ml. of 0.1 N potassium permanganate solution to 10 ml. of the sample and heat just to boiling on the steam bath for 10 min. Some pink color should remain at the end of this time if the material is within specification.

Literature References

1. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., Inc. (1937).
2. "Specifications for Analytical Reagents", American Chemical Society (1942).

Written by: A. Chetham-Strode
Date: July, 1952

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DETERMINATION OF RESIDUE

Gravimetric Method

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Principle

A weighed sample is volatilized in a tared crucible. The residue is weighed and the percent residue calculated.

Procedure - Analysis of Carbon Tetrachloride, Nitric Acid, and Trichloroethylene (Permachlor)

Accurately pipet 10 ml. of the sample into a tared 100 ml. platinum dish. (Remark 1) Continue with the general procedure.

Procedure - Analysis of Methanol

Accurately pipet 100 ml. of the sample into a tared 100 ml. platinum dish. (Remark 1) Continue with the general procedure.

Procedure - Analysis of Iodine

Accurately weigh 10 g. of the sample into a tared 100 ml. porcelain dish. Continue with the general procedure.

Procedure - Analysis of Oxalic Acid

Accurately weigh 5 g. of the sample into a tared porcelain crucible. Ignite to constant weight at a red heat, cool, and weigh (Remark 2).

Procedure - Analysis of Hydrofluorosilicic Acid

Accurately weigh 4 g. of the sample into a tared 100 ml. platinum dish. Add about 4 ml. of hydrofluoric acid and evaporate to dryness on a steam bath. Ignite to constant weight in a furnace at 600°-800°C, cool, and weigh.

Procedure - General

Evaporate the sample ~~to~~ dryness on a steam bath (Remark 3). Dry in an oven at 105° - 110°C, ~~cool~~, ~~and~~ weigh.

Calculations

$$\% \text{ Residue} = \frac{\text{g. residue} \times 100}{\text{g. sample}}$$

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Remarks

1. A 10 ml. sample gives the following sample weights:

carbon tetrachloride	16.0 g.
trichloroethylene	14.6 g.
60% nitric acid	13.7 g.
70% nitric acid	14.0 g.
95% nitric acid	14.9 g.

A 100 ml. sample gives the following sample weight:

methanol	79.6 g.

2. The ignited residue from this analysis should be reserved for iron determination.

3. The solid iodine sample should be sublimed to a minimum residue before drying.

Literature References

1. Rosin, "Reagent Chemicals and Standards", D. Van Nostrand Co., Inc., (1937).

2. "Specifications for Analytical Reagents", American Chemical Soceity, (1941).

Written by: A. Chetham-Strode
Date: July, 1952

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DETERMINATION OF HEATING VALUE

Calorimetric Method

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Principle

A bomb containing a known weight of sample in an atmosphere of oxygen is submerged in a known weight of water. The charge is ignited electrically. The heat liberated in the combustion is measured by noting the temperature rise of the water in the jacket. Using the specific heat of water, the heat liberated may be calculated. The result is corrected for the heat absorbed by the calorimeter, the combustion product, and the combustion of the fuse wire.

Although water is formed as one of the combustion products, additional water is added to saturate the dry oxygen gas. The water is needed to insure the complete formation of nitric and sulfuric acids from their respective anhydrides which are formed during the combustion reaction. The total amount of acid formed is determined by titration and this result used to correct the calorimeter determination for the heat absorbed by the water and nitric acid formed. The sulfate correction is obtained independently by the precipitation of barium sulfate which is weighed.

Apparatus

Parr oxygen bomb
Calorimeter

Solution

Standardized sodium carbonate, 0.0767 N. Weigh accurately 4.064 g. of anhydrous sodium carbonate into a one liter volumetric flask. Dissolve in 100 ml. of water. Dilute to mark with water and mix thoroughly. (1 ml = 2 BTU)

Procedure - Analysis of Coal

Assemble the electrode as shown in figure 1 using exactly 10 cm. of fuse wire.

Weigh accurately 1.0 g. of sample into a clean fuel capsule (Remark 1). Place capsule and contents under the loop electrode (Remark 2) of the bomb and add 1 ml. of distilled water. Assemble the bomb and fill with oxygen to a gauge pressure of 20 atmospheres (Remark 3).

Weigh exactly 2000 g. of water having a temperature 2.5°F below the room temperature, into the bucket. Place the bomb in the bucket and assemble the calorimeter.

After allowing the stirrer to run 5 min. at 150 rpm, record the temperature at 1 min. intervals for 5 min. (Remark 4). Close the switch keeping it closed until the pilot light goes off or for 5 seconds whichever is shorter. One minute after firing, record the temperature at 30 sec. intervals up to the point of maximum temperature and for 5 min. thereafter (Remark 4).

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Dismantle the calorimeter, releasing the pressure from the bomb slowly to prevent loss of condensed vapors. Remove bomb head (Remark 5) and wash all interior parts of the bomb into an Erlenmeyer flask using 0.08% methyl orange solution for washing. Titrate the washings with the standardized 0.0767 N sodium carbonate to a color change from orange to yellow. Record the volume of titrant used.

After completing the titration, add 1 ml. of concentrated ammonium hydroxide. Filter the precipitate from the solution. Wash precipitate and filter paper several times with water. Add 10 ml. of saturated bromine water to the filtrate. Make the solution slightly acidic with 1:1 hydrochloric acid. Boil until all bromine is expelled as indicated by a permanent pink color after the addition of a drop of 1% methyl orange solution. Neutralize the solution to the methyl orange endpoint (yellow color) with a clear saturated sodium carbonate solution. Acidify with 2 ml. of 1 M hydrochloric acid. Boil a few minutes to expel the carbon dioxide and add 10 ml. of 10% barium chloride. Continue heating at boiling temperature for 15 min. After allowing to stand 2 hrs., filter through an ignited and tared Gooch crucible. Wash the crucible and contents with water. Dry the crucible and contents at 105°C for 1 hr. and ignite at 900-950°C to constant weight. Determine a reagent blank for sulfate on the reagents used in the sulfate determination (Remark 6).

Carefully remove the unburned pieces of fuse wire and measure their total length in centimeters.

Standardize the calorimeter to determine the calorimeter factor using a weighed-1 g. sample of standard benzoic acid or standard calorific mixture in place of the coal sample using the procedure for the analysis of coal.

Calculations

Sulfur

$$\% \text{ sulfur} = \frac{(A - B) \times 0.1374 \times 100}{\text{g. sample}}$$

A = g. of barium sulfate precipitate
B = g. of barium sulfate blank

Corrections

Acid correction (BTU) = 2 x ml. 0.0767 N sodium carbonate
Wire correction (BTU) = 5 x (initial length - final length)
Sulfur correction (BTU) = 23 x % sulfur x g. of sample
Total correction (BTU) = acid correction + wire correction + sulfur correction

Calorimetric factor from benzoic acid

$$F = \frac{1.8 \times A \times B + C}{\Delta T}$$

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A = g. of benzoic acid
B = cal/g., heat of combustion of benzoic acid
C = Total correction (BTU)
ΔT = Final temperature - initial temperature

Calorimeter factor from standard calorific mixture $= F = \dfrac{D \times E \times 0.002205 + C}{\Delta T}$

D = g. of calorific mixture
E = BTU/lb heat of combustion of calorific mixture

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Heating value of coal

$$\text{BTU/lb} = \frac{F \times \Delta T - C}{\text{g. sample} \times 0.002205}$$

F = calorimetric factor

Remarks

1. The fuel capsule must be clean. Clean off any adhering particles with emery cloth and ignite capsule at 600°C until free of carbonaceous material. Handle capsule with tweezers and store in a stoppered bottle.

2. If a powdered sample is used, better results are obtained if the fuse wire is set slightly above the surface of the sample. If a sample pellet is used, the wire must touch the pellet with enough force to hold the pellet securely in place.

3. Do not flush the air present out of the bomb, since a small amount of nitrogen catalyzes the reaction.

4. Use a telescopic lens at right angles to the stem to avoid errors in parallex. Tap the thermometer lightly before each reading to be sure menicus is not sticking. This is of especial importance when the mercury is falling. Three constant readings at the initial and final temperatures are regarded as the temperature used in the calculations. These temperatures are corrected for calibration errors using the Bureau of Standard correction curve supplied with the thermometer.

5. If soot or unburned carbon is observed on the interior surface of bomb, reject and repeat the determination.

6. The result from this determination may be reported as % sulfur in sample.

References

1. "Methods of Analyzing Coal and Coke", Bureau of Mines Technical Paper No. 8, (1938).

2. "Standard Methods for the Sampling and Analysis of Coal and Coke", A.S.T.M. Standards, 1940 Supplement, Part III, pp. 1-21.

Written by: R. E. Ewing
Date: July, 1952

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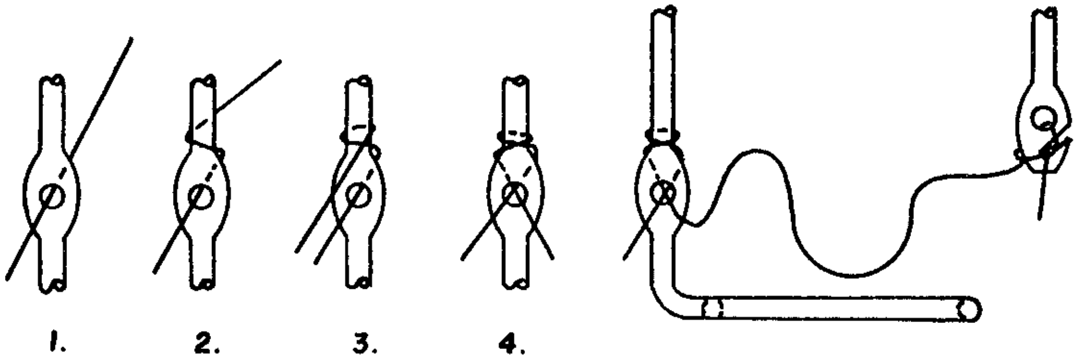
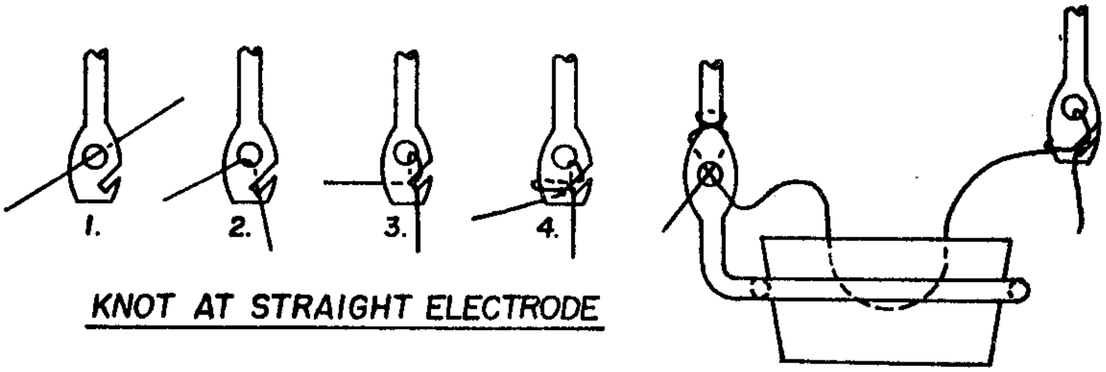


KNOT AT LOOP ELECTRODE

ELECTRODE PREPARED FOR CAPSULE



KNOT AT STRAIGHT ELECTRODE

ELECTRODES AND CAPSULE

FUSE WIRE DETAILS

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DETERMINATION OF PARTICLE SIZE

Sieve Method

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Principle

A sample is placed in the top of a nest of U.S. sieves and the sieves are shaken for a definite period of time. The residue in each sieve is weighed and the percentage passing or retained is calculated.

Procedure - Analysis of Lime

Use U.S. standard sieves #20 and #100. Proceed as described in the general procedure.

Procedure - Analysis of Iron Powder

Use U.S. standard sieves #100, #200, and #325. Proceed as described in the general procedure.

Procedure - Analysis of Sodium Bismuthate

Use U.S. standard sieve #200. Proceed as described in the general procedure.

Procedure - Analysis of Super Filtrol

Use U.S. standard sieves #10, #100, and #325. Proceed as described in the general procedure.

Procedure - General

Weigh 100 g. of sample to the nearest 0.1 g. and place on the top sieve. Place sieves in Ro-Tap Shaker and shake for 30 minutes. Weigh residue on each sieve.

Calculations

% passing on 1st screen = 100 (a)
% passing on 2nd screen = 100 (a + b)
% passing on 3rd screen = 100 (a + b + c)

where a = weight on first screen
b = weight on second screen
c = weight on third screen

Literature Reference

1. Griffins, "Technical Methods of Analysis", pp. 814-815, (1927).

Written by: Jeanette Watkins
Date: July, 1952

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DETERMINATION OF GASES

Gas Method

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Principle

The method consists of taking a measured volume of gas sample, removing various components one by one by suitable reactions, and measuring the decrease in volume caused by each removal. Results are reported on a percentage basis.

The apparatus is equipped with a compensator tube which compensates for any temperature and pressure changes; so the entire analysis is carried out at constant pressure.

Carbon monoxide and hydrogen are both oxidized in the copper oxide tube. The contraction in volume immediately following the oxidation is the measure of the volume of hydrogen in the sample. The carbon dioxide is then absorbed; the contraction in volume is the measure of the amount of carbon monoxide present.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$O_2 + \text{Alk. Pyrogallol} \longrightarrow \text{Oxidation Products}$$

$$H_2 + CuO \xrightarrow{290\text{-}310^\circ C} Cu + H_2O$$

$$CO + CuO \xrightarrow{290\text{-}310^\circ C} Cu + CO_2$$

The amount of nitrogen in helium is not determined with this apparatus; however, knowing the density of the helium sample and the volume fractions of the other impurities, volume percent nitrogen is calculated.

Solutions

Potassium hydroxide, 37.5% solution.
Alkaline pyrogallol. Pour a solution of 100 g. of potassium hydroxide in 200 ml. of water into a 250 ml. glass-stoppered bottle containing 10 g. of solid pyrogallis acid and mix.

Apparatus

Fisher Gas Analyzer, Unitized Model.
Pipets: 1. 37.5% potassium hydroxide for the removal of carbon dioxide, 2. alkaline pyrogallol solution for the absorption of oxygen.

Procedure - Analysis of Helium, Nitrogen, Hydrogen, Argon, Carbon Monoxide, Carbon Dioxide and Oxygen

Introduction of Sample

Have 10-15 ml. of pure inert gas; such as nitrogen, in the buret. This could be inert gas left from a previous analysis. Connect the sampling tube to the

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buret stopcock and purge the connecting tube allowing the gas to escape through the manifold. After purging, turn the buret and copper oxide tube stopcocks and flush the manifold and copper oxide tube with the pure nitrogen from the buret. Raise the mercury in the buret until the bore of the stopcock is filled and then immediately close the stopcock at the end of the manifold. Turn the buret stopcock with its bore full of mercury and draw in the gas to be analyzed. Measure the volume of sample and continue as under "Analysis of Carbon Dioxide and Oxygen" or as under "General".

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Procedure - Analysis of Carbon Dioxide and Oxygen

Draw in the proper amount of pure nitrogen and store in the alkaline pyrogallol pipet. Draw in the sample and measure. Dilute the sample by introducing the nitrogen from the pipet to the buret. Close off the manifold, and thoroughly mix the gas by raising and lowering the leveling bulb several times. Read the volume of the mixture.

Procedure - General

To make a separation, establish communication between the buret and the proper pipet. Force the gas into the pipet by raising the leveling bulb until the mercury reaches the capillary stem at the top of the buret. Then draw the gas back into the buret by lowering the leveling bulb. Repeat the operation until there is no further contraction in volume. Finally, draw the reagent up to the reference mark, close off the stopcock to the pipet, and read the volume. In this manner separate carbon dioxide in the alkali pipet, then oxygen in the pyrogallol pipet.

Treat the sample in the copper oxide tube and determine the volume change due to combustion of hydrogen and carbon monoxide. Have the tube at 290°-310°C and pass the sample through it at 10-15 ml/min. Repeat the treatment and finally measure the volume.

Pass the gas again through the alkali pipet to separate the carbon dioxide formed by combustion and measure the volume.

Calculations

$$\text{Volume \% component}_{(CO_2, O_2, H_2)} = \frac{\text{Decrease in Volume}}{\text{Volume of Sample}} \times 100$$

$$\text{Volume \% CO} = \frac{\text{Volume of } CO_2 \text{ formed}}{\text{Volume of Sample}} \times 100$$

Volume % $N_2 = 100 \times fN_2$ (used only to determine nitrogen in helium)

$$fN_2 = \frac{do-(1-fO_2-fH_2-fCO_2)dHe-(dO_2 \times fO_2)-(dH_2 \times (fH_2)-(dCO_2 \times fCO_2)}{dN_2 - dHe}$$

$$fN_2 = \frac{do-(1-fO_2-fH_2-fCO_2)0.1785-(1.4290 \times fO_2)-(0.0899 \times fH_2)-(1.9642 \times fCO_2)}{1.2506 - 0.1785}$$

do = Density of gas sample; determined by gas density analysis
fO_2 = Decimal volume fraction of oxygen; determined by gas analysis
fH_2 = Decimal volume fraction of hydrogen; determined by gas analysis
fCO_2 = Decimal volume fraction of carbon dioxide; determined by gas analysis
dHe = Density of helium; obtained from handbook
dO_2 = Density of oxygen; obtained from handbook
dH_2 = Density of hydrogen; obtained from handbook
dCO_2 = Density of carbon dioxide; obtained from handbook
dN_2 = Density of nitrogen; obtained from handbook

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Remarks

A thin film of water is necessary over the mercury in the buret to saturate the sample with water vapor.

The densities of all gases used in the formula for the calculation of nitrogen in helium are constant. All percentages should be converted to whole numbers before multiplying.

Literature References

1. "Burrell Manual for Gas Analysts", Burrell Technical Supply, Pittsburgh, Pa., Ed. 4.

2. Altieri, V. J., "Gas Analysis and Testing of Gaseous Materials", American Gas Association, Inc., (1945).

3. Matuszak, M. P., "Fisher Gas - Analysis Manual", 3rd Rev. Ed., Fisher Scientific Co., Pittsburgh, Pa.

Written by: K. Koyama
Date: July, 1952

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DETERMINATION OF DENSITY

Gas Method

Principle

A measured volume of the gas sample is taken, and its temperature, pressure, and weight are determined. The density at standard conditions is calculated in grams per liter.

Apparatus

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High vacuum system; see drawing.

Procedure - Analysis of Helium

Evacuation of System. Close stopcocks 3 and 5; open all others. Start the vacuum pump, then slowly open s.c. 3 and bring the mercury in A to the stopcock. Surround trap T_1 with a mixture of dry ice-acetone. Place the diffusion pump, P, into operation and continue to evacuate for 30 min.

Calibration of Flask, F. After the evacuation procedure, close s.c. 1 and 6; then remove sample flask F. Remove the grease from the joint on F, wipe the flask with a chamois, and weigh on a semi-micro balance, using a similar size flask as a tare. Fill the flask with clean, dry air and reweigh. Note the barometric pressure and the temperature.

Calculations

$$V_f = 2.1513 \times \frac{WT}{P}$$

where V_f = Volume of flask F
W = Wt. of air
T = Temperature of air, degrees absolute
P = Barometric pressure, mm. of mercury.

Analysis of Sample

Allow the system to evacuate for 15 min. under the evacuation procedure with the calibrated flask F in position. Note the pressure on manometer M and the temperature. Attach a rubber hose to the sample cylinder and equip the other end of the hose with a short glass "U" tube. Purge the hose with sample and place the "U" tube in the sample receiving flask, A. Displace two-thirds of the mercury by allowing the sample to enter slowly.

Close s.c. 4 and open s.c. 3 slowly to allow the sample to enter the system. Record the pressure on manometer M. Close s.c. 1 and 6; weigh the flask as under the calibration procedure.

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Calculations

$$do = 2.7818 \times \frac{WT}{U_f (P_1 - P_2)}$$

do = density, g./l., S.T.P.
W = wt. of sample, g.
T = temp. of sample, degrees absolute
P_1 = initial pressure reading, mm.
P_2 = final pressure reading, mm.
V_f = volume of density flask.

Literature References

1. Restricted report: "The Procedure for the Determination of Gas Densities", R. N. Smith to L. W. Safranski, April 30, 1945.

Written by: K. Koyama
Date: July, 1952

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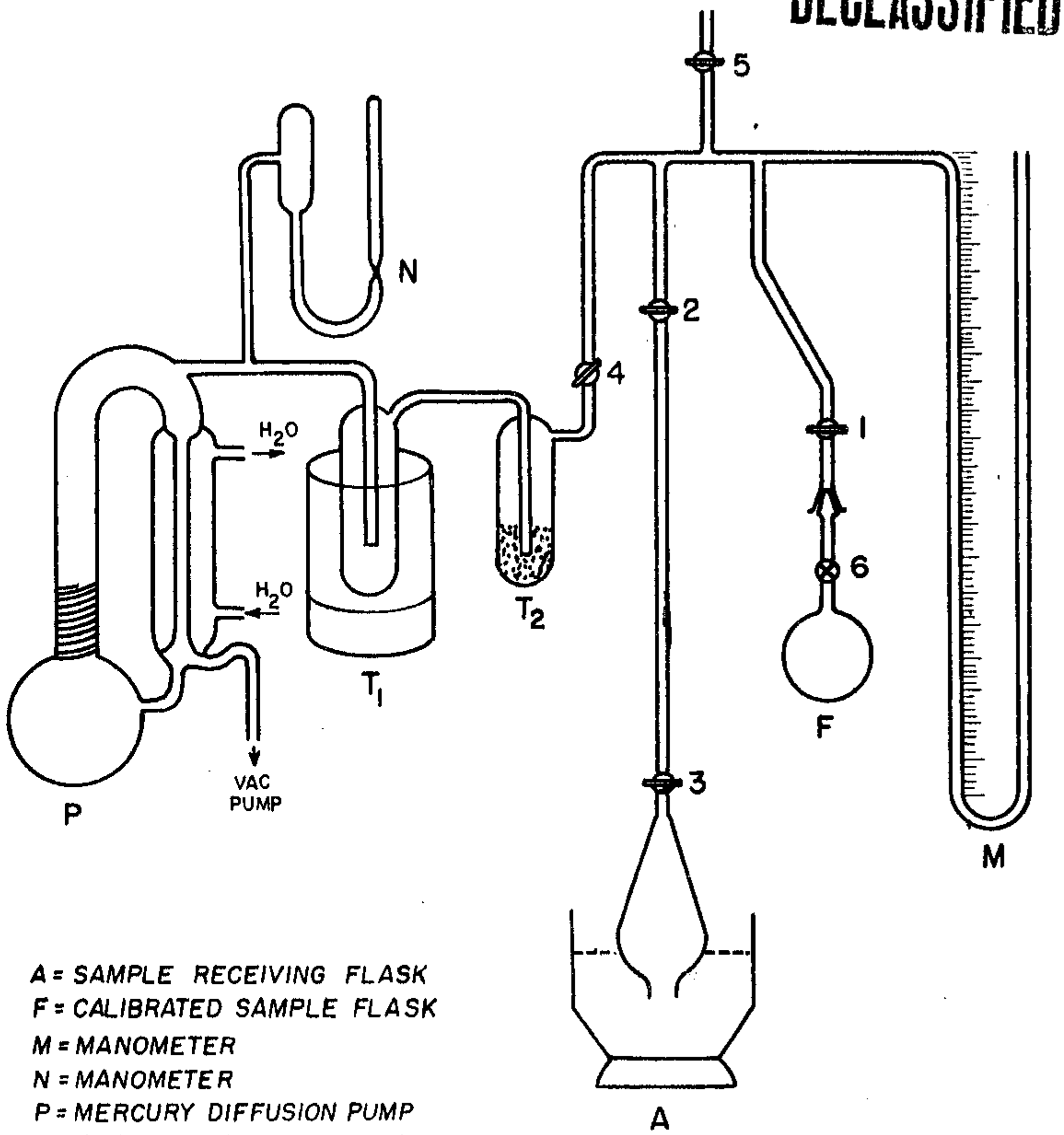

A = SAMPLE RECEIVING FLASK
F = CALIBRATED SAMPLE FLASK
M = MANOMETER
N = MANOMETER
P = MERCURY DIFFUSION PUMP
T_1 = TRAP, DRY ICE - ACETONE
T_2 = TRAP, GOLD TURNINGS

GAS DENSITY APPARATUS

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DETERMINATION OF WATER IN GASES

Gas Method

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Principle

The gas to be analyzed is passed through an absorption tube containing anhydrone which will quantitatively absorb water. The volume of sample is the amount of water displaced in an aspirator bottle. The gain in weight of the absorption tube is calculated to a volume percentage of the sample.

Procedure - Analysis of Helium, Hydrogen, Nitrogen and Oxygen

Pass about 50 ml. of the gas sample through the absorption tube; then wipe and weigh.

By means of a short rubber tube, connect one end of the absorption tube to the sample cylinder and the other end to the water aspirator which has been filled with water saturated with the gas sample. Collect 1000 ml. of displaced water at a flow rate of about 25 ml. per min. Remove the absorption tube, wipe, and weigh. The gain in weight is the amount of water.

Calculations

$$\text{Volume \% } H_2O = \frac{\text{g. of water} \times 22{,}400 \times 100}{18 \times \text{ml. of sample}}$$

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Date: July, 1952

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Code Zz-21

DETERMINATION OF IMPURITIES

Spectrographic Method

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Principle

Analysis is accomplished by exciting the sample in a direct current arc, evaluating the intensity of the impurity emission lines, and comparing the latter with those of standard samples.

Apparatus

Emission spectrograph, source, and densitometer.

Procedure - Analysis of Hydrogen Peroxide

Evaporate ten ml. of sample to about one ml., and add to 500 mg. of pure uranous-uranic oxide (U_3O_8). Dry, ignite at 750°C, and analyze by the carrier concentration method. Determine Fe, Sn, and P.

Procedure - Analysis of Calcium

To one g. of sample, add dropwise slightly more water than required to effect conversion to calcium hydroxide. Evaporate the excess water and ignite at 750°C for one hour. Grind the resulting oxide in a mortar. Mix a portion of the ground material with 5% of pure gallium oxide.

For the determination of B, Be, and Cu, pellet 25 mg. of the gallium oxide mixture and place the pellet in a crater electrode. For the determination of Li, Na, Mg, Al, Si, Mn, Cr, Co, Ni, and Fe, use 10 mg. of the mixture.

Excite the sample at 12 amp.(short circuit) with the direct current arc. Compare the resultant spectra with those produced with pure matrix material to which known amounts of impurities (as solutions) have been added.

Procedure - Analysis of Magnesium Oxide

To convert the fused sample to a soft form, dissolve one g. in silica-distilled nitric acid, dry, and ignite at 750°C. Grind the resulting oxide in a mortar.

Prepare mixtures indicated below for the required determinations:

Element Line	Sensitivity, ppm	Sample mixture and weight
Al 3082, 3093	1	1:20:20 Ga_2O_3, MgO, graphite powder; 20 mg.
B 2497	1	MgO; 10 mg.
Be 3131	1	MgO; 10 mg.
K 7665	10	1:20 Ga_2O_3, MgO; 10 mg.
Li 6707	1	1:20 Ga_2O_3, MgO; 10 mg.
Na 5890, 5896	1	1:20 Ga_2O_3, MgO; 10 mg.

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Excite the sample at 12 amp. (short circuit) with the direct current arc. Compare the resultant spectra with those produced with pure matrix material to which known amounts of impurities (as solutions) have been added.

Procedure - Analysis of 2S Aluminum Cans, Caps, Ingots, Aluminum Dummies HW 117, Al-Si

Clean surface of sample and arc by means of the AC arc directly using a counter-electrode of graphite; arcing current to be 6.5 amperes. Determine by densitometry and calculate the percentages of the following elements as needed, B, Si, Ni, Bi, Al, Fe, Mg, Cu, Pb, Sn, Cr, Mn, Ti, Zn, Cd, Co.

Suitable standards may be obtained from the Aluminum Company of America.

Procedure - Analysis of Nitric Acid

Add 10 ml. of the sample to 100 mg. of pure zinc oxide and evaporate to dryness. Ignite the residue at 750°C for one hour, grind in a mortar, and mix with an equal weight of graphite powder by further grinding. Place 20 mg. portions of the mixture in a 3 mm. crater electrode (Fig. 1, page Zz-22-3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the spectra with those prepared with pure zinc oxide containing known amounts of the impurity elements.

The analysis lines and their sensitivities are given in Remark 1.

Procedure - Analysis of Hydriodic Acid

Add 10 ml. of the sample to 100 mg. of pure zinc oxide, evaporate to dryness, add 1 ml. of nitric acid, and heat until the evolution of iodine ceases. Ignite the residue at 750°C for one hour, grind in a mortar, and mix with an equal weight of graphite powder by further grinding. Place 20 mg. portions of the mixture in a 3 mm. crater electrode (Fig. 1, page Zz-22-3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the spectra with those prepared with pure zinc oxide containing known amounts of the impurity elements.

The analysis lines and their sensitivities are given in Remark 1.

Procedure - Analysis of Oxalic Acid

Mix 10 g. of the sample with 100 mg. of zinc oxide and heat until decomposition of the oxalic acid is completed. Ignite the residue at 750°C for one hour, grind in a mortar, and mix with an equal weight of graphite powder by further grinding. Place 20 mg. portions of the mixture in a 3 mm. crater electrode (Fig. 1, page Zz-22-3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the spectra with those prepared with

Excite the sample at 12 amp. (short circuit) with the direct current arc. Compare the resultant spectra with those produced with pure matrix material to which known amounts of impurities (as solutions) have been added.

Procedure - Analysis of 2S Aluminum Cans, Caps, and Ingots

Collect about 30 mg. of filings from the sample with a double-cut second cut file. Mix and place three mg. of the filings on a freshly pre-arced platform electrode (see drawing in reference 2). Add about 25 ul. of sucrose solution (160 mg./ml. in a mixture of one part ethanol to four parts water), and gently tap the base of the electrode to disperse the filings evenly over the surface of the liquid. Evaporate the liquid and arc the sample at 12 amp. short circuit. Determine by densitometry and calculation the percentage of Cu, Fe, Mg, Mn, and Si in the sample.

Suitable standards may be obtained from the Aluminum Company of America.

Procedure - Analysis of Nitric Acid

Add 10 ml. of the sample to 100 mg. of pure zinc oxide and evaporate to dryness. Ignite the residue at 750°C for one hour, grind in a mortar, and mix with an equal weight of graphite powder by further grinding. Place 20 mg. portions of the mixture in a 3 mm. crater electrode (Fig. 1, page Zz-22-3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the spectra with those prepared with pure zinc oxide containing known amounts of the impurity elements.

The analysis lines and their sensitivities are given in Remark 1.

Procedure - Analysis of Hydriodic Acid

Add 10 ml. of the sample to 100 mg. of pure zinc oxide, evaporate to dryness, add 1 ml. of nitric acid, and heat until the evolution of iodine ceases. Ignite the residue at 750°C for one hour, grind in a mortar, and mix with an equal weight of graphite powder by further grinding. Place 20 mg. portions of the mixture in a 3 mm. crater electrode (Fig. 1, page Zz-22-3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the spectra with those prepared with pure zinc oxide containing known amounts of the impurity elements.

The analysis lines and their sensitivities are given in Remark 1.

Procedure - Analysis of Oxalic Acid

Mix 10 g. of the sample with 100 mg. of zinc oxide and heat until decomposition of the oxalic acid is completed. Ignite the residue at 750°C for one hour, grind in a mortar, and mix with an equal weight of graphite powder by further grinding. Place 20 mg. portions of the mixture in a 3 mm. crater electrode (Fig. 1, page Zz-22-3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the spectra with those prepared with

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pure zinc oxide containing known amounts of the impurity elements. The analysis lines and their sensitivities are given in Remark 1.

Remarks

1.

Element Line	Sensitivity, ppm	HNO_3	HI	$(COOH)_2 \cdot 2H_2O$
Al 3082, 3093	0.1	x	x	x
As 2780	5.	x	x	
B 2497	1.	x	x	x
Be 3131	0.1	x	x	x
Fe 2628	0.1	x	x	
Li 6707	0.1	x	x	x
Mg 2852	0.1	x	x	x
Na 5890, 5896	0.1	x	x	x
P 2535, 2553	1.		x	
Si 2507	0.1	x	x	x

Procedure - Analysis of Bronze Flux

Grind one gram of the flux in an agate mortar until a fine powder is obtained. Weigh 10 milligrams of the powdered flux into a crater electrode. Excite the sample at 12 amps (short circuit) with a direct current. Compare the resultant spectra with those produced with pure matrix material to which known amounts of lithium have been added.

Remarks

Element Lines -- Li 6104, 6708

Sensitivity -- 50 ppm (0.005%).

References

1. Daniel, J.L., Heim, M.L., and Olund, E.L., "Analytical Procedures for the Plutonium Metal Fabrication Process, II. Spectrochemical Analysis of Essential Materials," Document HW-25170 (1952)(Confidential).

2. Hasler, M.F., Harvey, C.E., and Dietert, H.W., Ind. Eng. Chem., Anal. Ed., 15, 102 (1943).

3. Letter A.J. Zeitz to E.P. Galbraith, Aug. 6, 1953, entitled, "Determination of Lithium in Flux Consisting of Barium Chloride, Potassium Chloride, and Sodium Chloride."

Written by: L.F. Kendall
Revised: September, 1953

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Obsolete as of Sept. 1953
Date

pure zinc oxide containing known amounts of the impurity elements.

The analysis lines and their sensitivities are given in Remark 1.

Remarks

1.

Element Line	Sensitivity, ppm	HNO_3	HI	$(COOH)_2 \cdot 2H_2O$
Al 3082, 3093	0.1	x	x	x
As 2780	5.	x	x	
B 2497	1.	x	x	x
Be 3131	0.1	x	x	x
Fe 2628	0.1	x	x	
Li 6707	0.1	x	x	x
Mg 2852	0.1	x	x	x
Na 5890, 5896	0.1	x	x	x
P 2535, 2553	1.		x	
Si 2507	0.1	x	x	x

References

1. Daniel, J.L., Heim, M.L., and Olund, E.L., "Analytical Procedures for the Plutonium Metal Fabrication Process, II. Spectrochemical Analysis of Essential Materials," Document HW-25170 (1952)(Confidential).

2. Hasler, M.F., Harvey, C.E., and Dietert, H.W., Ind. Eng. Chem., Anal. Ed., 15, 102 (1943).

Written by: L. F. Kendall
Date: August, 1952

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DETERMINATION OF BORON

Spectrographic Method

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Principle

Excitation with the direct current arc produces a spectrum from which boron may be determined semi-quantitatively by comparison with spectra of suitable standards.

Apparatus

Emission spectrograph, source, and densitometer.

Procedure - Analysis of Metso "99" and Nacconal N.R.

Place ten mg. of the sample in a three mm. deep crater in a 1/4" dia. graphite electrode. Arc at 12 amp. (short circuit) with the direct current arc. Determine the amount of boron present by comparing the resulting spectrograms with those of suitable standards.

Procedure - Analysis of Nitric Acid

Add 200 mg. of calcium oxide to 3 ml. of water and 0.25 ml. of the sample, and evaporate to dryness. Convert the residue to the oxide by igniting at 750°C for one hour. Grind the oxide in a mortar and mix a portion of the sample with 5% gallium oxide by grinding. Place 10 mg. of the mixture in a 3 mm. crater electrode (Fig. 1, page 3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the resulting spectra with those of pure calcium oxide to which known amounts of boron have been added.

Procedure - Analysis of Hydriodic Acid

Add 200 mg. of calcium oxide to 3 ml. of water and 0.25 ml. of the sample, and evaporate to dryness. Then add 1 ml. of nitric acid, and heat until the evolution of iodine ceases. Convert the residue to the oxide by igniting at 750°C for one hour. Grind the oxide in a mortar and mix a portion of the sample with 5% gallium oxide by grinding. Place 10 mg. of the mixture in a 3 mm. crater electrode (Fig. 1, page 3) and excite at 12 amp. (short circuit) with the direct current arc. Compare the resulting spectra with those of pure calcium oxide to which known amounts of boron have been added.

Procedure - Analysis of Oxalic Acid

Mix 375 mg. of the sample with 200 mg. of calcium oxide and 5 ml. of water, evaporate to dryness, and continue heating until decomposition of the oxalic acid is completed. Convert the residue to the oxide by igniting at 750°C for one hour. Grind the oxide in a mortar and mix a portion of the sample with 5% gallium oxide by grinding. Place 10 mg. of the mixture in a 3 mm. crater electrode (Fig. 1, page 3) and excite at 12 amp. (short circuit) with

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August, 1952

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the direct current arc. Compare the resulting spectra with those of pure calcium oxide to which known amounts of boron have been added.

References

1. Daniel, J.L., Heim, M.L., and Olund, E.L., "Analytical Procedures for the Plutonium Metal Fabrication Process, II. Spectrochemical Analysis of Essential Materials," Document HW-25170, (1952)(Confidential).

Written by: L. F. Kendall
Date: August, 1952

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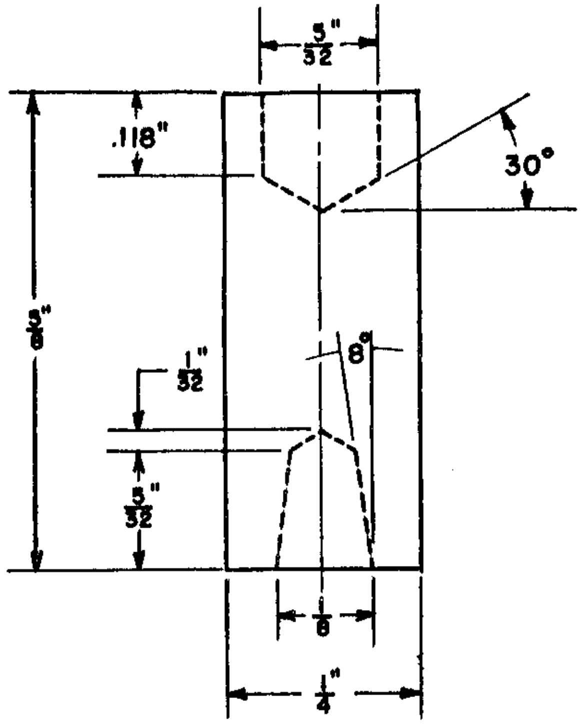
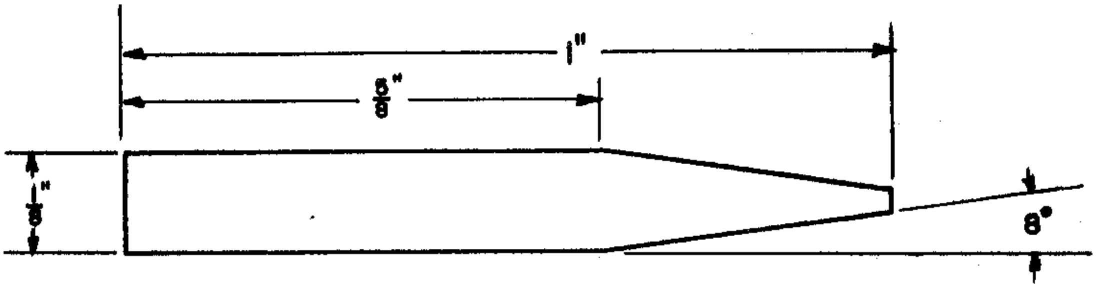


ANODE CAP-.118" CUP



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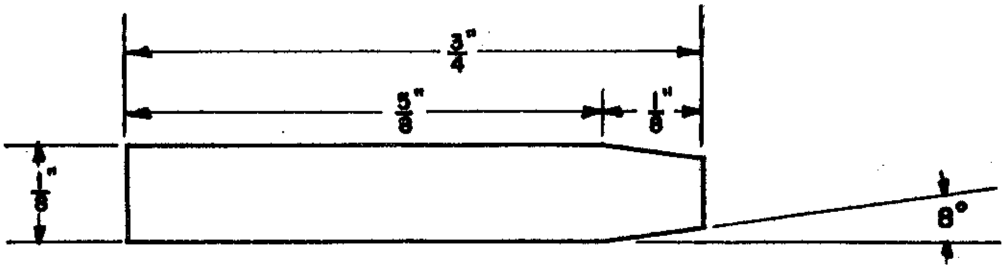

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August, 1952

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ELECTRODE SHAPES

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