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Wet Chemical Methods for Analyzing Taconite, Iron Ore, and Metallurgical Products

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WET CHEMICAL METHODS FOR ANALYZING TACONITE, IRON ORE, AND METALLURGICAL PRODUCTS

by

W. T. Westbrook,[1] R. H. Jefferson,[2] and A. L. Birr[1]

ABSTRACT

This Bureau of Mines report contains methods for analyzing iron ore for total iron, ferrous iron, metallic iron, silica, manganese, aluminum, calcium, magnesium, phosphorus, titanium, carbon, sulfur, moisture loss, and ignition loss by wet chemical methods. Some are modifications of standard umpire methods; others have been developed by the Bureau of Mines to provide a combination of speed and accuracy. They are suitable for a high volume of samples and/or control situations, and for situations in which instrumental results must be verified. These methods have been used to analyze taconites, native ores, some foreign ores, and metallurgical products.

INTRODUCTION

Iron is the basic metal employed in modern industry. The United States produces approximately 10% of the world's iron ore, of which about 80% is from the Lake Superior region.

Prior to 1950, most of the iron ore mined and shipped from the Lake Superior region was direct-shipping ore, high-grade material with an iron content of more than 60%. As a result of increasingly large-scale production, resources of direct-shipping ore were rapidly being depleted; therefore, it became necessary to obtain alternate sources. This led to efforts to bring the large reserves (some estimated at over 5 billion tons) of taconite into production.

Taconite is metamorphosed, low-grade, fine-grained iron ore produced by chemical sedimentation. It is commonly, but not necessarily, laminated with chert (finely crystallized quartz), and the iron may exist in the form of carbonates, silicates, oxides, or sulfides. The iron oxides--hematite, magnetite, and goethite--are the most economically significant rock types because the iron content commonly ranges from 25% to 40%, and because they are more easily concentrated. The formations are generally low in alumina, sodium, and potassium, but may contain appreciable amounts of manganese, magnesium, and calcium.

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[1] Chemist.

[2] Supervisory chemist.

The use of perchloric acid is significant in most of the methods; however, alternatives are included for use in laboratories where the use of perchloric acid would not be feasible.

ACKNOWLEDGMENTS

This publication is a compilation of analytical methods developed and implemented in the Twin Cities Metallurgy Research Center, and the former Metallurgy Research Laboratory in Bruceton, Pa. These methods were developed over a period of many years. During that time, D. J. Kusler and E. A. Hattman, both supervisory chemists at the Bruceton Laboratory, and A. L. Whiting, supervisory chemist at the Twin Cities Metallurgy Research Center, were instrumental in developing and modifying many of these procedures.

EXPERIMENTAL PROCEDURES

Total Iron

The determination of iron in iron ore is almost always made by titrating the sample with a standard solution of either potassium dichromate or potassium permanganate.

The potassium dichromate method (7, 13)[3] is based on the oxidation of the ferrous salts to the ferric state with potassium dichromate. Barium diphenylamine sulfonate is the internal indicator; it gives an intense blue-violet color in the presence of a slight excess of the oxidant.

Reagents

Potassium Dichromate Solution.--(0.1 N) Dissolve 4.904 grams of the salt in H_2O and dilute to 1 liter. Standardize the solution with a standard iron ore (NBS standard iron ore or equivalent).

Stannous Chloride Solution.--Dissolve 150 grams $SnCl_2 \cdot 2H_2O$ in 300 ml HCl conc and dilute to 1 liter with H_2O.

Phosphoric Acid-Sulfuric Acid Mixture.--Mix 15 ml H_2SO_4 with 300 ml H_2O. Cool, then add 150 ml H_3PO_4, and dilute with H_2O to 1 liter.

Mercuric Chloride.--Saturated solution of $HgCl_2$ (60-70 grams per liter of H_2O).

Sodium Peroxide.--Granular.

Perchloric Acid.--Concentrated.

Hydrofluoric Acid.--Concentrated.

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Calculation

Determine the gram equivalence of iron for 1.0 ml $K_2Cr_2O_7$ by analyzing a standard iron ore.

$$\frac{\%\ \text{Fe in standard ore} \times \text{wt of standard}}{\text{Volume of } K_2Cr_2O_7} = \text{g eq Fe/ml of } K_2Cr_2O_7$$

Determine the percentage of iron in the unknown sample.

$$\frac{\text{g eq Fe} \times \text{volume of } K_2Cr_2O_7 \text{ to titrate unknown}}{\text{wt of sample}}\ 100 = \%\ \text{Fe}$$

Example:

66.60% = percentage of iron in NBS standard iron ore 27e

0.5 g = weight of standard

0.5 g = weight of unknown

37.70 ml = volume of $K_2Cr_2O_7$ to titrate standard

29.35 ml = volume of $K_2Cr_2O_7$ to titrate unknown sample

$$\frac{0.6660 \times 0.5\ \text{g}}{31.7} = 0.0105\ \text{g eq Fe/ml } K_2Cr_2O_7$$

$$\frac{0.0105 \times 29.35}{0.5\ \text{g}} \times 100 = 61.66\%\ \text{Fe in unknown}$$

Ferrous Iron

An accurate determination of ferrous iron presents many difficulties, and is sometimes impossible to obtain. Grinding the sample in air lowers the FeO and increases the Fe_2O_3 (8, p. 907). Dissolving the sample without taking special precautions to maintain an inert atmosphere leads to further oxidation. The presence of metallic iron, organic matter, or decomposable sulfides cause high results. If the material contains manganese dioxide, chlorine will be liberated and will oxidize the ferrous iron, causing low results (13). Several methods exist for determining ferrous iron, but all are inapplicable if materials are present that can be oxidized by the titrating agent. Sulfides, pyrite, organic matter (other than free carbon), and metallic iron are all included in this group of inteferences.

Ferrous Iron in the Absence of Metallic Iron

This method for determining ferrous iron provides speed, reasonable accuracy, and precision without special apparatus or equipment.

Potassium Dichromate.--Same as used for total iron.

Phosphoric Acid-Sulfuric Acid Mixture.--Same as used for total iron.

Hydrofluoric Acid.--Concentrated.

Hydrochloric Acid.--Concentrated.

Barium Diphenylamine Sulfonate Indicator.--Same as used for total iron.

Reflux flask with a ground-glass top.

Reflux condenser.

Electric hot plate.

Acetone.

Procedure

1. Weigh 0.5 gram of a finely ground iron ore sample and transfer it to a 500-ml refluxing flask containing boil chips or beads.

2. Mix exactly 5 ml of bromine and 100 ml of methanol in a beaker and add to the refluxing flask. Swirl; immediately connect the flask to the reflux condenser.

3. Heat to a low boil on an electric plate and boil for 15 min.

4. Remove the flask from the plate, and disconnect the condenser and stopper immediately. Cool to room temperature.

5. Filter through medium paper (Whatman No. 30).[5] Wash the flask and filter paper with methanol until all of the brown-colored iron bromide is removed. Finally, wash once or twice with acetone.

6. Return the paper and residue to the flask and add approximately 1 gram NA_2CO_3 and 40 ml HCl. Add a few drops HF. Heat rapidly until the sample is in solution, about 3 to 5 min.

7. Filter through a thin, glass-wool mat to remove most of the filter paper. Receive the filtrate in a 600-ml beaker containing 300 ml of cold H_2O, 25 ml of the H_3PO_4-H_2SO_4 mixture, and 10 drops of indicator.

8. Titrate with standard $K_2Cr_2O_7$ until a constant blue-violet end-point is obtained.

9. Calculate the same as for total iron.

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[5]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

water, so the resulting silica contains fewer contaminants. When sulfuric acid is used, there exists the danger of forming insoluble, or only slightly soluble, salts of elements such as barium, calcium, lead, etc.

Reagents

Dilute Hydrochloric Acid.--1:1. Add one volume of acid to an equal volume of H_2O.

Hydrochloric Acid.--Concentrated.

Nitric Acid.--Concentrated.

Perchloric Acid.--Concentrated.

Dilute Sulfuric Acid.--1:1. Add one volume of acid to an equal volume of H_2O.

Hydrofluoric Acid.--Concentrated.

Procedure

1. Weigh a 0.5- to 1.0-gram sample and transfer to a 400-ml beaker.

2. Digest in 50 ml of dilute HCl. When the sample is in solution, add 15 ml HNO_3, and 40 ml $HClO_4$ (or 25 ml H_2SO_4).

3. Dehydrate to fumes of $HClO_4$, and continue heating for at least 10 min.

4. Cool the sample, add 15 ml HCl conc, dilute to 100 ml with hot H_2O and filter through rapid filter paper (Whatman No. 541), retaining the filtrate. Wash the precipitate with dilute HCl and finally with hot H_2O.

5. Put the precipitate into a platinum crucible. All of the silica is not removed by a single dehydration; therefore, a second dehydration of the filtrate should be made by repeating steps 3 and 4, and adding the silica to the first precipitate.

6. Heat the crucible, and ignite its contents in a muffle furnace to 1,000° C.

7. Weigh the crucible and record the weight. Moisten the crucible contents and add 2 to 4 drops of dilute H_2SO_4 and about 15 ml HF.[6]

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[6]The SiO_2 contains small amounts of contaminants that cannot be removed by washing (9). The H_2SO_4 oxidizes these contaminants, which would be erroneously weighed as fluorides, or prevents volitization of titanium or zirconium fluorides if they are present in the sample.

4. Bring the solution to a boil on the hot plate, and heat until $HClO_4$ fumes develop and a refluxing action is evident; continue fuming the sample for 10 min. The dehydrated SiO_2 will precipitate as the boiling progresses, but it must not be allowed to bake to the bottom of the beaker. (The 10-min fuming time is important because if the SiO_2 is not completely dehydrated, it will be very difficult to filter and might cause low results.)

5. After fuming, cool the sample, then add 15 ml HCl conc. Break up the congealed mass, add 100 ml of hot H_2O and filter through fast, acid-hardened filter paper (Whatman No. 541). Police the beaker and wash the residue thoroughly with dilute HCl, and then hot H_2O in order to remove iron and other contaminants from the dehydrated SiO_2.

6. Burn off in a clay crucible at 1,000° C to constant weight. Weigh directly as SiO_2 (9, p. 394).

$$\frac{\text{Wt of residue}}{\text{Wt of sample}} \times 100 = \% \ SiO_2$$

NOTE.--Some authorities, such as Kolthoff and Sandell (9, p. 388), indicate that glass beakers cannot be used in the determination of silica, that a double dehydration is necessary, and that the silica must also be treated with hydrofluoric acid. These accommodations are necessary for very accurate determinations, but for many control situations and for less precise work, this method produces reliable results, since 99% of the silica is recovered by a single dehydration in glass beakers. Treating with hydrofluoric acid is necessary only when the color of the precipitate indicates contamination.

Manganese

Two methods for determining manganese are considered: (1) the persulfate method (1, 8, p. 446), and (2) the modified Lingane method (12).

Persulfate Method

This method involves the oxidation of Mn^{2+} to the permanganate state by using ammonium persulfate with silver nitrate as a catalyst.

Reagents

Manganese Dissolving Acid.--Add 100 ml H_2SO_4 to 525 ml H_2O. Cool, and add 125 ml H_3PO_4 and 250 ml HNO_3.

Silver Nitrate Solution.--Dissolve 8 grams $AgNO_3$ in 1 liter H_2O.

Sodium Arsenite Solution.--Dissolve 3.7 grams $NaAsO_2$ in 1 liter H_2O. Standardize with a sample of known manganese content.

Ammonium Persulfate (25% solution).--Dissolve 25 grams $(NH_4)_2S_2O_8$ salt in 75 ml H_2O.

Reagents and Apparatus

Potassium Permanganate Solution.--Dissolve 2.0 grams $KMnO_4$ crystals in 1 liter of H_2O. Allow solution to stand in a lightproof container for at least 24 hours; filter through fitted glass, and standardize against a standard manganese sample of similar composition.

Saturated Sodium Pyrophosphate.--40 grams $Na_4P_2O_7$ in 1 liter H_2O.

Sodium Hydroxide.--Dissolve 250 grams in H_2O and dilute to 1 liter. Store in a polyethylene bottle.

Dilute Hydrochloric Acid.--(1:1). Add a volume of acid to an equal volume of H_2O.

pH-Millivoltmeter.--A variety of instruments, either separate or combined, can be used to make the pH adjustment and to measure the voltage during titration.

Hydrochloric Acid.--Concentrated.

Nitric Acid.--Concentrated.

Procedure

1. Dissolve a 0.5-gram sample of iron ore in a 400-ml beaker with 15 ml HCl conc and 15 ml HNO_3. Add a few drops HF and evaporate to dryness. Redissolve the sample in 15 ml HCl conc and again evaporate to dryness.

2. Add 2 ml HCl conc and wash all of the sample to the bottom of the beaker with 10 to 20 ml H_2O.

3. Add 150 ml of saturated $Na_4P_2O_7$ solution; adjust pH to between 6.5 and 7.0 with either dilute HCl or 25% NaOH.

4. Switch the selector control of the meter to the millivolt mode and titrate to the potentiometric end-point with $KMnO_4$.

Calculation

$$\frac{\%\ \text{Mn in standard} \times \text{wt of standard}}{\text{volume of } KMnO_4} = \text{g eq of Mn/ml of } KMnO_4$$

$$\frac{\text{g eq of Mn} \times \text{volume of } KMnO_4}{\text{wt of sample}} \times 100 = \%\ \text{Mn}$$

Aluminum

Accurate aluminum determinations (13, p. 576) can be difficult to obtain for a number of reasons, some of which are (1) incomplete decomposition of

4. Add NaOH to the filtrate until iron starts to precipitate; add dilute H_2SO_4 dropwise until the solution becomes clear; then add 5 ml in excess.

5. Transfer the solution to a mercury cathode cell and electrolyze to the absence of iron as indicated by the following spot test: Put a drop of the sample solution on a spot plate, and test with the potassium ferrocyanide-potassium ferricyanide indicator. If a blue color appears when drops of the solution and indicator are combined on the plate, iron is still present. If it remains colorless, the iron has been completely removed. If calcium and magnesium are to be determined, samples that are fumed with $HClO_4$ must be evaporated to dryness after the iron has been removed in order to expel the $HClO_4$. This is necessary because $HClO_4$ will interfere with the determination of calcium and magnesium.

6. Transfer the iron-free solution to a 400-ml beaker, add 10 ml of HCl conc, and heat to near boiling. Add NH_4OH dropwise until the solution reaches a methyl red end-point (yellow color), and then add 2 or 3 drops in excess.

7. Digest for 1 to 2 min. Keep the solution ammonical and filter through a rapid paper (Whatman No. 541), saving the filtrate and washings for determining calcium and magnesium. Wash thoroughly with the 5% NH_4Cl solution. Ignite in a weighed platinum crucible to 1,000° C. Treat with HF to eliminate silica, reignite to 1,000° C, and weigh as Al_2O_3.[8]

$$\frac{\text{wt of residue}}{\text{wt of sample}} \times 100 = \% \ Al_2O_3$$

An alternating method for getting the sample into solution has been developed by the Eberbach Corp. in its DynaCath Working Manual (5). It is as follows:

1. Weigh a 1.0-gram sample into a 250-ml beaker. Add 25 ml of HCl conc and digest on hot plate (adding more HCl if necessary) until action ceases. Add a few drops of HNO_3 and evaporate to 2 to 3 ml.

2. Cool, add 10 ml HCl conc, digest, and transfer to a platinum dish. Add 5 ml of dilute H_2SO_4, 10 ml HF, and evaporate to heavy fumes.

3. Cool the dish and leach the contents with hot water, keeping the volume less than 100 ml. Any insoluble residue must be filtered and fused with Na_2CO_3 and added to the filtrate. Proceed with step 4 of the ammonium hydroxide method.

Ammonium Phosphate Method

With the ammonium phosphate method (13, p. 350), it is not necessary to remove iron before precipitating aluminum. Sodium thiosulphate is added to reduce the iron and hold it in solution.

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[8] The precipitate is crude Al_2O_3, possibly containing TiO_2, V_2O_5, and P_2O_5.

Reagents

EDTA Solution.--Dissolve 4 grams of the disodium salt in 1 liter H_2O. Standardize with a material of known composition prepared in the same manner as the sample. A standard combining 0.25-gram-weight each of National Bureau of Standards No. 1a (limestone) and No. 88 (dolomite) has been used successfully.

Potassium Hydroxide.--20% aqueous solution.

Potassium Cyanide.--10% aqueous solution.

Modified Calcium Indicator Powder.--Mix thoroughly 0.2 gram of calcein (4) with 0.12 gram of thymol pthalein and 20.0 gram of potassium chloride.

Dilute Sulfuric Acid.--1:1. Add a volume of acid to an equal volume of H_2O.

Ammonium Chloride.--20% aqueous solution.

Ammonium Persulfate.--25% aqeous solution.

Procedure

Take the filtrate retained from the ammonium hydroxide determination of aluminum, dilute it to 300 ml, and proceed to step 5 of the method. If this is not available, the following may be substituted:

1. Transfer a 0.5- to 1.0-gram sample to a 400-ml beaker. Wet thoroughly with water, and add 25 ml of HCl conc.

2. Digest the sample until the action ceases. Add 5 ml HNO_3 conc, 10 ml dilute H_2SO_4, and evaporate until fumes of H_2SO_4 appear. (Dense fumes above the liquid in the beaker.) Cautiously, dilute to about 50 ml with hot H_2O and filter through moderate paper (Whatman No. 40), retaining the filtrate. Wash the residue thoroughly with hot H_2O.

3. Transfer the paper and contents to a platinum crucible and ignite in a muffle furnace or over a blast burner. Cool the crucible, wet the contents, and add 3 or 4 drops dilute H_2SO_4 and 15 ml HF. Evaporate slowly to dryness.

4. Add 5 grams Na_2CO_3 and fuse. Leach this melt and add it to the filtrate. Make the solution acid with dilute H_2SO_4 and add 5 ml in excess. Transfer the solution to the mercury cathode and electrolyze until nearly all iron is removed.[9] The solution need not be completely free of iron by the spot test as in the determination of aluminum. Transfer the solution to a 400-ml beaker.

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[9]If the mercury cathode is not available, precipitate the sample twice to insure complete removal of calcium.

Indicator.--Dissolve 0.15 gram of Eriochrome black T and 0.5 gram of sodium borate in 25 ml of methanol (or ethanol).

Procedure

1. Pipet a 25-ml aliquot from the 500-ml volumetric flask into a beaker.

2. Add, in order, 5 to 6 ml of buffer solution, several drops of KCN, and 5 or 6 drops of the indicator solution. The color of the solution should be wine-red. If not, add more buffer solution, 1 ml at a time.

3. Titrate to a pure blue. A white surface is the better background for indicating the end-point of this titration.

Calculation

This titration represents the volume of EDTA required for both calcium and magnesium; therefore, subtract the volume required for the lime titration from the total titration in order to determine the volume of EDTA required for magnesium oxide. Calculate total magnesium as magnesium oxide by using the factor obtained from a standard sample carried through the same procedure.

$$\frac{\%\ MgO\ in\ standard \times wt\ of\ standard}{Total\ Titration - CaO\ Titration} = g\ eq\ of\ MgO/ml\ of\ EDTA$$

$$\frac{g\ eq\ MgO \times volume\ of\ EDTA\ (Total\ Titration - CaO\ Titration)}{wt\ of\ sample} \times 100 = \%\ MgO$$

Titanium

The most common method for determining titanium is the colorimetric method (8, p. 581), based on the yellow or amber color produced by the reaction of hydrogen peroxide and titanium in a dilute sulfuric or perchloric acid solution.

Some elements interfere with the determination because of the color of their solutions, such as iron, nickel, or chromium. Other elements interfere by reacting with hydrogen peroxide to form colored compounds (for example, vanadium, molybdenum, and cerium); others (such as fluorine, phosphates, and large quantities of alkali salts) bleach the color developed by peroxide. For all practical purposes, these interferences are eliminated by evaporating the sample to heavy fumes of sulfuric or perchloric acid, and measuring the absorbence of the sample containing peroxide against an equal aliquot free of hydrogen peroxide.

Reagents and Apparatus

Hydrochloric Acid.--Concentrated.

Perchloric Acid.--Concentrated.

successfully in determining microamounts (less than 0.01% phosphorus). The gravimetric method has also been used to make determinations of phosphorus microamounts, but is more accurate above 0.1%. The gravimetric method is presented with two variations.

Colorimetric Determination (the Molybdenum Blue Reaction) (7)

Reagents and Apparatus

Sodium Sulfite.--10% solution prepared fresh daily.

Sodium Carbonate.--Granular.

Hydrazine Sulfate.--0.15% solution prepared fresh daily.

Ammonium Molybdate Solution.--Add 300 ml H_2SO_4 conc to 500 ml H_2O, and cool to room temperature. Dissolve 20 grams of ammonium molybdate in the H_2SO_4 solution, and dilute to 1 liter with H_2O.

Color Development Reagent.--Dilute 25 ml of the ammonium molybdate solution with 45 ml H_2O. Add 10 ml of the hydrazine sulfate solution and 20 ml of the sodium sulfite solution, and dilute to 100 ml with H_2O. This reagent is stable for only about 30 min; therefore, it must be prepared as needed.

Spectrophotometer.--With red photo tube.

Perchloric Acid.--Concentrated.

Methyl Red.--Indicator solution.

Procedure

1. Weigh a 0.5-gram sample and transfer it to a large platinum crucible containing about 5.0 grams Na_2CO_3. Mix thoroughly. Cover with another 2.0 grams Na_2CO_3. Add 7.0 grams Na_2CO_3 to another crucible and carry it through the same procedure as a reagent blank. Fuse the sample and the blank for 20 to 30 min. Carefully pour the molten charge into a 400-ml beaker containing 200 ml of cold H_2O. (Alternatively, the charge may be poured into a platinum dish and then transferred to the beaker.)

2. Heat slowly until the fused mass disintegrates. Filter through medium paper (Whatman No. 30) into a 400-ml beaker. Add several drops of methyl red indicator and make the solution acid with $HClO_4$. Boil the solution gently to expel CO_2 and transfer it to a 250-ml volumetric flask. Adjust it to volume, take a 25-ml aliquot and put this aliquot into a 125-ml Erlenmeyer flask along with 4 ml $HClO_4$.

3. Evaporate the contents of the flask until $HClO_4$ fumes reach the mouth of the flask. Cool, wash down the insides of the beaker with about 10 ml H_2O, and evaporate to fumes again.

5. Cool to 60° C, then add 20 ml HNO_3 conc and 60 ml of Johnson's molybcate solution, and shake for 10 min. Wash down the sides of the flask and allow to stand at least 4 hours, but preferably overnight.

6. Filter through a weighed, fitted glass crucible, wash with 1% HNO_3 and dry at 105° to 110° C for 90 min.

7. Reweigh the crucible. The precipitate is ammonium phosphomolybdate.

$$\frac{\text{Wt of residue}}{\text{Wt of sample}} \times 1.63 = \% \text{ P } (13, \text{ p. } 225)$$

Gravimetric Determination (Without the Use of Perchloric Acid) (13, p. 535)

Reagents

Molybdic Acid Solution.--This solution is prepared in two parts and then the two are combined. Solution 1--dissolve 50 grams of molybdic acid in 120 ml H_2O and 80 ml NH_4OH conc. Stir vigorously, and filter when solution is complete. Solution 2--combine 300 ml HNO_3 and 470 ml H_2O. Slowly add solution 1 to solution 2 with a funnel extending to the bottom of the container. Mix thoroughly.

Hydrochloric Acid.--Concentrated.

Sodium Carbonate.--Granular.

Nitric Acid.--Concentrated.

Ammonium Hydroxide.--Concentrated.

Dilute Ammonium Hydroxide.--1:1. Add 1 volume of concentrated HN_4OH to an equal volume of H_2O.

Nitric Acid.--0.5% solution.

Potassium Nitrate.--0.5% aqueous solution.

Procedure

1. Weigh a 1.0-gram sample and put it into a beaker. Wet thoroughly with H_2O and add 25 ml HCl. Digest slowly.

2. Evaporate the sample to dryness, and bake. Redissolve with 10 ml HCl and 25 ml hot H_2O.

3. Filter through moderate paper (Whatman No. 30), and burn off in a platinum crucible. Fuse the insoluble residue with Na_2CO_3, and combine this with the filtrate in a 250-ml Erlenmeyer flask.

Procedure

1. After assembling and testing the apparatus for a continuous and unrestricted flow of oxygen through the system (approximately 0.5 liter per minute), run a blank by burning 1.0 gram of iron chips and 0.5 gram of copper. Allow the oxygen to flow through the bulb for 15 min and weigh.

2. Transfer a 0.5- to 1.0-gram sample into a crucible containing approximately 0.5 gram of iron chips. Add 0.5 to 1.0 gram more of the iron chips and 0.5 gram more of the copper. (A scoop is available, or can be made, that holds approximately 0.5 gram.) Put the crucible into the combustion chamber and start the furnace. Insure that the burn cycle is complete. Turn off power and continue oxygen flow for at least 3 min.

3. Weigh the absorption bulb. The increase in weight represents CO_2.

4. Remove the crucible and examine it to insure complete combustion.

$$\frac{(\text{Wt increase} - \text{correction for blank}) \times 0.2729}{\text{wt of sample}} \times 100 = \% \text{ C}$$

Sulfur

Sulfur (2, p. 158; 11) is converted to SO_2, which is titrated with KIO_3 solution.

Reagents and Apparatus

Furnace.--An induction furnace capable of heating samples to 1,500° C.

Combustion Crucible and Cover.--Sulfur-free.

Accelerator.--Analyzed copper and/or tin, and iron chips. Approximately 1 gram of iron is needed to insure proper operation of the induction furnace and complete burning of the sample.

Oxygen.--Bubble 1 liter per minute through a column containing H_2SO_4 to remove H_2O.

Sulfur Determinator.--Models are available that provide for either manual or automatic operation.

Potassium Iodate.--0.207 gram of KIO_3 in 1 liter of water. Determine the gram equivalent of the solution by analyzing a standard sample.

Starch Solution.--Add 2 grams of arrowroot starch to 50 ml H_2O. Stir this into 150 ml H_2O containing 6 grams KI and bring to a boil, stirring constantly. Cool and store in a polyethylene dispenser.

Hydrochloric Acid Solution.--Add 15 ml HCl conc to 1 liter H_2O.

Calculation

The percentage of moisture is the difference between the first and second weights multiplied by 100.

(1st wt of crucible and sample - 2d wt) X 100 = % moisture

The percentage of ignition loss is the difference between the first and third weights multiplied by 100.

(1st wt of crucible and sample - 3d wt) X 100 = % ignition loss.

Example:

1.0 gram = wt of the sample.

22.6347 = wt of crucible and sample.

22.6132 = wt of crucible and sample after heating 2 hours at 105° C.

22.5852 = wt of crucible and sample after heating 4 hours at 1,000° C.

22.6347 gram	22.6347
-22.6132 gram	-22.5852
0.0215 X 100 = % moisure.	0.0495 X 100 = % ignition loss.

CONCLUSIONS

Methods for the determination of the following have been presented: total iron, ferrous iron, metallic iron, silica, manganese, aluminum, calcium, magnesium, phosphorus, titanium, carbon, sulfur, moisture loss, and ignition loss.

Total iron was determined volumetrically by titration with potassium dichromate. Ferrous iron was determined by dissolving the sample in hydrochloric and hydrofluoric acids in a carbon dioxide atmosphere produced by the addition of sodium carbonate to the sample, and then titrating as in total iron. Metallic iron was dissolved by mercuric chloride, filtered, and titrated with potassium dichromate.

Silica was determined gravimetrically. The sample was fused with sodium peroxide in an iron crucible, dehydrated with perchloric acid, ignited in a clay crucible, and weighed as silica. Dehydration may be done with sulfuric acid; however, it is more time-consuming because of the care that must be exercised in reducing sulfuric acid to a low volume. Also, when sulfuric acid is used, the residue should be ignited in a platinum crucible and treated with hydrofluoric acid.

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