



# Standard Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass<sup>1</sup>

This standard is issued under the fixed designation C 169; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 These test methods cover the quantitative chemical analysis of soda-lime and borosilicate glass compositions for both referee and routine analysis. This would be for the usual constituents present in glasses of the following types: (1) soda-lime silicate glass, (2) soda-lime fluoride opal glass, and (3) borosilicate glass. The following common oxides, when present in concentrations greater than indicated, are known to interfere with some of the determinations in this method: 2 % barium oxide (BaO), 0.2 % phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>), 0.05 % zinc oxide (ZnO), 0.05 % antimony oxide (Sb<sub>2</sub>O<sub>3</sub>), 0.05 % lead oxide (PbO).

1.2 The analytical procedures, divided into two general groups, those for referee analysis, and those for routine analysis, appear in the following order:

	Sections
Procedures for Referee Analysis:	
Silica	10
BaO, P <sub>2</sub> O <sub>5</sub> (Al <sub>2</sub> O <sub>3</sub> + P <sub>2</sub> O <sub>5</sub> ), CaO, and MgO	11-15
Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub> by Photometry and Al <sub>2</sub> O <sub>3</sub> by Complexometric Titration	16-22
Cr <sub>2</sub> O <sub>3</sub> by Volumetric and Photometric Methods	23-25
MnO by the Periodate Oxidation Method	26-29
Na <sub>2</sub> O by the Zinc Uranyl Acetate Method and K <sub>2</sub> O by the Tetraphenylborate Method	30-33
SO <sub>3</sub> (Total Sulfur)	34 to 35
As <sub>2</sub> O <sub>3</sub> by Volumetric Method	36-40
Procedures for Routine Analysis:	
Silica by the Single Dehydration Method	42-44
Al <sub>2</sub> O <sub>3</sub> , CaO, and MgO by Compleximetric Titration, and BaO, Na <sub>2</sub> O, and K <sub>2</sub> O by Gravimetric Method	45-51
BaO, Al <sub>2</sub> O <sub>3</sub> , CaO, and MgO by Atomic Absorption; and Na <sub>2</sub> O and K <sub>2</sub> O by Flame Emission Spectroscopy	52-59
SO <sub>3</sub> (Total Sulfur)	60
B <sub>2</sub> O <sub>3</sub>	61 to 62
Fluorine by Pyrohydrolysis Separation and Specific Ion Electrode Measurement	63-66
P <sub>2</sub> O <sub>5</sub> by the Molybdo-Vanadate Method	67-70
Colorimetric Determination of Ferrous Iron Using 1,10 Phenanthroline	71-76

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

## 2. Referenced Documents

2.1 ASTM Standards:<sup>2</sup>

C 146 Test Methods for Chemical Analysis of Glass Sand  
 C 225 Test Methods for Resistance of Glass Containers to Chemical Attack

D 1193 Specification for Reagent Water

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry

## 3. Significance and Use

3.1 These test methods can be used to ensure that the chemical composition of the glass meets the compositional specification required for the finished glass product.

3.2 These test methods do not preclude the use of other methods that yield results within permissible variations. In any case, the analyst should verify the procedure and technique employed by means of a National Institute of Standards and Technology (NIST) standard reference material having a component comparable with that of the material under test. A list of standard reference materials is given in the NIST *Special Publication 260*,<sup>3</sup> current edition.

3.3 Typical examples of products manufactured using soda-lime silicate glass are containers, tableware, and flat glass.

3.4 Typical examples of products manufactured using borosilicate glass are bakeware, labware, and fiberglass.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C14 on Glass and Glass Products and are the direct responsibility of Subcommittee C14.02 on Chemical Analysis.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from National Institute of Standards and Technology, Gaithersburg, MD 20899.

3.5 Typical examples of products manufactured using fluoride opal glass are containers, tableware, and decorative glassware.

#### 4. Purity of Reagents

4.1 Reagent grade chemicals shall be used throughout. Unless otherwise indicated, it is intended that reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type I, II, or III of Specification **D 1193**.

#### 5. Concentration of Acids and Ammonium Hydroxide

5.1 When acids and ammonium hydroxide are specified by name or chemical formula only, concentrated reagents of the following percent concentrations are intended:

	%
Hydrochloric acid (HCl)	36 to 38
Hydrofluoric acid (HF)	48 to 51
Nitric acid (HNO <sub>3</sub> )	69 to 71
Perchloric acid (HClO <sub>4</sub> )	70 to 72
Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	95 to 98
Ammonium hydroxide (NH <sub>4</sub> OH)	28 to 30

5.2 Concentrations of diluted acids and NH<sub>4</sub>OH except when standardized are specified as a ratio, stating the number of volumes of the concentrated reagent to be added to a given number of volumes of water, as follows: HCl (1 + 99) means 1 volume of concentrated HCl (approximately 37 %) added to 99 volumes of water.

5.3 The hygroscopic nature of the ignited precipitates of silica, aluminum oxide, and calcium oxide obtained in the methods to be described, requires the use of fresh and highly active desiccants. For this purpose, magnesium perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>) and barium oxide (BaO) are recommended.

#### 6. Filter Papers

6.1 Throughout these test methods, filter papers will be designated as “coarse,” “medium,” or “fine,” without naming brands or manufacturers. All filter papers are of the double acid washed ashless type. “Coarse” filter paper refers to the porosity commonly used for the filtration of aluminum hydroxide. “Medium” filter paper refers to that used for filtration of calcium oxalate, and “fine” filter paper to that used for barium sulfate.

#### 7. Photometers and Photometric Practice

7.1 Photometers and photometric practice prescribed in these methods shall conform to Practice **E 60**.

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2 The considerations of instrumentation given in Test Methods **C 146** are equally applicable to these test methods.

#### 8. Preparation of Sample

8.1 Glass crushed in a steel mortar as described in Test Methods **C 225**, and sieved through a 150- $\mu$ m (No. 100) mesh sieve, is generally suitable for analysis, except for the determination of iron oxide (Fe<sub>2</sub>O<sub>3</sub>). After crushing and sieving, place the powder on a sheet of paper and pass a small magnet through it to remove adventitious iron. Then store in a tightly closed container and keep in a desiccator.

8.2 A sample prepared in an iron mortar is not recommended for the determination of Fe<sub>2</sub>O<sub>3</sub>. Instead, glass should be ground in an agate mortar after ascertaining it is free of contamination.

8.3 A sample prepared for the determination of fluorine should be sieved through a 75- $\mu$ m (No. 200) mesh sieve rather than a 150- $\mu$ m (No. 100) sieve.

8.4 The practice of drying samples in a drying oven at 105 to 110°C after preparation is not recommended. Powdered glass can fix CO<sub>2</sub> and water as readily at this temperature as at room temperature. A freshly prepared sample, if exposed but a short time to the atmosphere, will not have acquired an ignition loss of much analytical significance. If ignition loss is determined, use the following temperature schedules:

Soda-lime glass, 800°C for 1 h  
 Fluorine opal glass, 500 to 550°C for 1 h  
 Borosilicate glass, 800°C for 1 h

Determine the ignition loss on a 1 to 3-g sample in a platinum crucible.

#### 9. Precision and Bias

9.1 The probable precision of results that can be expected by the use of the procedures described in these test methods is shown in the following tabulation. Precision is given as absolute error, and is dependent on the quantity of constituent present as well as the procedure used.

Constituent	Probable Precision of Results, weight %	
	Referee Analysis	Routine Analysis
Silica	±0.1	±0.25
BaO	±0.02	±0.05
Al <sub>2</sub> O <sub>3</sub> + P <sub>2</sub> O <sub>5</sub>	±0.05	±0.10 (–P <sub>2</sub> O <sub>5</sub> )
CaO	±0.05	±0.15
MgO	±0.05	±0.02 to 0.10
Fe <sub>2</sub> O <sub>3</sub>	±0.003	...
TiO <sub>2</sub>	±0.005	...
ZrO <sub>2</sub>	±0.001 to 0.005	...
Cr <sub>2</sub> O <sub>3</sub> (volumetric)	±0.005	...
Cr <sub>2</sub> O <sub>3</sub> (photometric)	±0.0001 to 0.001	...
MnO	±0.001 to 0.005	...
Na <sub>2</sub> O	±0.05	±0.25 (flame emission)
K <sub>2</sub> O	±0.02 to 0.05	±0.02 to 0.10 (flame emission)
SO <sub>3</sub>	±0.02	±0.05
As <sub>2</sub> O <sub>3</sub>	±0.005	...
P <sub>2</sub> O <sub>5</sub>	...	±0.005 to 0.02
B <sub>2</sub> O <sub>3</sub>	...	±0.05 to 0.15
Fluorine	...	±0.01 to 0.20 (0.1 to 6.0 %)

9.2 It is recommended that *reported* results be rounded as follows:

Percent	Number of Significant Figures Retained After Rounding	<0.01	1 or 2
1 to 100	3		
0.1 to 0.99	2		
0.01 to 0.09	1 or 2		

9.3 *Recorded* results should be carried to one more significant figure than required in 9.2.

## PROCEDURES FOR REFEREE ANALYSIS

### SILICA

#### 10. Procedure

10.1 Weigh 1.000 g of powdered sample and 1.5 g of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) for soda-lime glass, or 2.0 g of  $\text{Na}_2\text{CO}_3$  for borosilicate glass, into a clean 75-mL platinum dish (see 10.1.1); mix well with a platinum or Nichrome<sup>5</sup> wire. Tap the charge so it lies evenly in the bottom of the dish. Cover with platinum lid and heat first at a dull red heat over a clean oxidizing flame; gradually raise the temperature until a clear melt is obtained. Properly carried out, little or no spattering should occur and the fusion can be performed in 3 to 4 min. When melted, rotate the melt to spread it evenly over the bottom and lower sides of the dish, gradually withdrawing from the flame. Cover and cool to room temperature. During fusion, the dish should be handled at all times with platinum-tipped tongs and the fusion performed with a platinum (preferably 90 % platinum and 10 % rhodium alloy) or silica triangle.

10.1.1 To obtain accurate repeat weighings, platinum ware shall be kept scrupulously clean on the outside of the vessel as well as on the inside. It should be polished brightly with fine, round grain sand and protected from dirty surfaces. It is recommended that porcelain plates be used for cooling fusions, and that platinum be set on paper towels or other clean material during filtration.

10.2 Add 20 to 25 mL of HCl (1 + 1) (Note 1) under the platinum cover and digest on a steam bath or hot plate until the melt has completely disintegrated; it is also possible to digest the melt in the cold overnight. Police and rinse the lid with a fine jet of water; rinse down the sides of the dish and evaporate to dryness on a steam bath or under an infrared lamp. Keep the dish covered with a raised cover glass during evaporation. When evaporation is complete (Note 2) (absence of HCl), cool, drench the residue with 5 mL of HCl, and then add 20 mL of hot water. Digest for 5 min and filter through a 9-cm medium filter paper. Catch the filtrate in a 250-mL platinum dish. Transfer the precipitated silica to the filter with the aid of a policeman and a bit of paper pulp, and wash the precipitate and paper twelve times with hot 2 % HCl. Transfer the paper and precipitate to the dish used for fusion and dehydration and reserve for subsequent ignition. Wipe the stirring rod and the periphery of the funnel with a piece of damp filter paper and add to the dish containing the precipitate for ignition.

NOTE 1—Glasses containing fluorine in small amounts (less than 0.25 %) will not cause significant error. Glasses containing larger amounts of fluorine (for example, fluoride opals) are analyzed as above with this

exception: after the fusion has been made and before addition of the acid (see 10.2), add 10 mL of aluminum chloride ( $\text{AlCl}_3$ ) solution (10 mL = 200 mg of Al) to complex fluorine. If evaporation is made on a steam bath, it is difficult to dry the residue. It is suggested that final drying, before filtration, be made in a drying oven for 30 to 45 min at 105°C.

Results for  $\text{SiO}_2$  when analyzing fluorine opals may tend to be low by 0.2 to 0.3 %. For an alternative, but more lengthy procedure, consult *Applied Inorganic Analysis*.<sup>6</sup>

NOTE 2—Boron in amounts less than 5 %  $\text{B}_2\text{O}_3$  does not interfere. However, if boron is greater than 5 %, proceed to the point of completing the first dehydration (see 10.2), then add 20 mL of anhydrous methanol saturated with dry HCl (gas), and evaporate to dryness on an air bath or under an infrared lamp. Repeat once more before proceeding.

10.3 Evaporate the filtrate to dryness on the steam bath or under an infrared lamp. When dry, cool, drench with 10 mL of HCl (1 + 1) and again evaporate just to dryness; then bake in a drying oven at 105°C for 30 min. Cool, drench with 5 mL of HCl, and add 20 mL of hot water and a small bit of filter pulp. Digest hot for 5 min and filter through a 7-cm fine paper. Police the dish with the aid of a bit of paper pulp and wash precipitate and paper eight times with hot 2 % HCl. Transfer the paper and precipitate to the dish containing the initial precipitation. Wipe the stirring rod and the periphery of the funnel with a piece of damp filter paper and add to the dish containing the precipitate for ignition.

10.4 Partially cover the dish with its platinum lid but leave enough space so air can circulate during ignition. Place the dish in a cold muffle furnace and bring the temperature to 1200°C for 30 min. Carefully and completely cover the dish before removing it from the furnace and transfer to a desiccator. Cool to room temperature and weigh the covered dish ( $W_1$ ). Moisten the silica with 1 to 2 mL of water and add 4 to 5 mL of HF and 0.5 g of oxalic acid crystals. Evaporate to dryness on a sand bath or under an infrared lamp. Carefully sublime any remaining oxalic acid, cover the dish with its platinum cover, heat to 1000°C for 2 min, cool, and weigh ( $W_2$ ) as before.

10.5 *Calculation*—Calculate the percent of  $\text{SiO}_2$  as follows:

$$\text{SiO}_2, \% = (W_1 - W_2) \times 100 \quad (1)$$

### BaO, $\text{R}_2\text{O}_3(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5)$ , CaO, AND MgO

#### 11. General Considerations

11.1 The detailed analysis described below may be desirable only infrequently. Several steps may be omitted without undue loss of accuracy, for example, the hydrogen sulfide ( $\text{H}_2\text{S}$ ) and the cupferron precipitations. Many glasses contain insignificant amounts of BaO (less than 0.1 %), in which case BaO also may

<sup>5</sup> Trademark of the Driver-Harris Co., 308 Middlesex St., Harrison, NJ 07029

<sup>6</sup> Hillebrand, Lundell, Bright, and Hoffman, *Applied Inorganic Analysis*, John Wiley & Sons, Inc., New York, NY, 1953, pp. 943–944.



be ignored. Thus, if the separation of BaO and the H<sub>2</sub>S precipitation are bypassed, the analysis can begin with the ammonia precipitation of the R<sub>2</sub>O<sub>3</sub> group. Frequently, correction of the R<sub>2</sub>O<sub>3</sub> for Fe<sub>2</sub>O<sub>3</sub>, titanium dioxide (TiO<sub>2</sub>), and zirconium oxide (ZrO<sub>2</sub>) will allow a useful estimation of the remainder as aluminum oxide (Al<sub>2</sub>O<sub>3</sub>); phosphoric anhydride (P<sub>2</sub>O<sub>5</sub>) is usually small (less than 0.02 %). However, if chromic oxide (Cr<sub>2</sub>O<sub>3</sub>) is present, it will be counted as Al<sub>2</sub>O<sub>3</sub>; for example, in some green glasses, Cr<sub>2</sub>O<sub>3</sub> may be as much as 0.25 %. H<sub>2</sub>SO<sub>4</sub> is preferred to HClO<sub>4</sub> in sample preparation when Cr<sub>2</sub>O<sub>3</sub> is present (0.01 to 0.25 %). The scheme of analysis is the same with either acid, except that BaO (if present) must be precipitated when HClO<sub>4</sub> is used, whereas it is rendered insoluble with the use of H<sub>2</sub>SO<sub>4</sub>.

## 12. Determination of BaO

12.1 Prepare the sample by using one of the following two methods:

12.1.1 *Using HClO<sub>4</sub>*—Weigh 2.000 g of sample into a 75 or 100-mL platinum dish, moisten with 5 mL of water, and add 10 to 12 mL of HF and 12 to 15 mL of HClO<sub>4</sub> while stirring with a platinum or plastic rod. Evaporate uncovered until fluorides begin to react, then cover with a platinum lid, allowing just sufficient space for HF to escape. When all reaction has subsided, cool, rinse off the lid and the sides of the dish, stir, and evaporate to strong fumes of HClO<sub>4</sub>. Cool, rinse down the sides of the dish, add 5 mL of saturated boric acid (H<sub>3</sub>BO<sub>3</sub>) solution, and evaporate to near dryness. Cool, and add 20 mL of water and 1 mL of HCl. Digest until salts have dissolved and transfer to a 250-mL beaker. If a small amount of insoluble material remains, police the dish and transfer any residue to the beaker. (In the absence of barium, proceed directly to precipitation with H<sub>2</sub>S or NH<sub>4</sub>OH.) Dilute to 100 mL and heat to a gentle boil. Precipitate barium by the slow addition of 10 mL of a 10 % solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or 2 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1). Digest near boiling for 1 h, cool, and allow to stand for 2 h. Filter through a 7-cm fine paper into a 400-mL beaker; police the beaker in which the precipitation was made with the aid of a bit of filter paper pulp. Wash 4 to 5 times with cold water containing a few drops of H<sub>2</sub>SO<sub>4</sub>. Reserve the filtrate (A). Proceed to 12.2.

12.1.2 *Using H<sub>2</sub>SO<sub>4</sub>*—Weigh 2.000 g of the sample into a 75 or 100-mL platinum dish, moisten with 5 mL of water, and add 12 to 15 mL of HF, 5 to 6 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1), and, if Cr<sub>2</sub>O<sub>3</sub> is present, 5 to 10 drops of H<sub>2</sub>SO<sub>3</sub> while stirring with a platinum or plastic rod. Evaporate uncovered until fluorides begin to react, then cover with a platinum lid, allowing just sufficient space for HF to escape. When the reaction has subsided, cool, rinse off the lid and the sides of the dish, and evaporate to strong fumes of H<sub>2</sub>SO<sub>4</sub>. Cool, rinse down the sides of the dish, add 2 mL of saturated H<sub>3</sub>BO<sub>3</sub> and 1 to 2 mL of HNO<sub>3</sub>; evaporate to dryness. Cool, add 5 mL of HCl and 20 mL of hot water, digest to disintegrate the salts, transfer to a 250-mL beaker, dilute to 150 mL, and boil gently for about 5 min to dissolve all sulfates except barium. (In the absence of barium, proceed directly to precipitation with H<sub>2</sub>S or NH<sub>4</sub>OH.) When all sulfates have dissolved except barium, adjust the acidity by neutralizing with NH<sub>4</sub>OH (using methyl red as the indicator) and reacidify with 1 mL of HCl. Add 3 to 4 drops of

H<sub>2</sub>SO<sub>4</sub> and digest hot for 30 min; cool for 2 h and filter through a fine 7-cm paper into a 400-mL beaker. Police the beaker with the aid of a bit of paper pulp and wash 4 to 5 times with cold water containing a few drops of H<sub>2</sub>SO<sub>4</sub>. Reserve the filtrate (A). Proceed to 12.2.

NOTE 3—An alternative procedure may be used to prepare the sample by first evaporating with HF alone. If evaporation is done at a moderate heat, it has the advantage of being allowed to proceed unattended. When the fluoride residue is dry, cover the dish with a platinum lid so as to allow sufficient space for vapors to escape. Add 10 to 12 mL of HClO<sub>4</sub> or 5 to 6 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1) underneath the lid, return to the source of heat, and after all fluorides have reacted, and mild fuming of HClO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub> has begun (usually in 10 min), cool, rinse the lid and sides of the dish with water, and continue the evaporation as described in 12.1.1 or 12.1.2.

12.2 Transfer the BaSO<sub>4</sub> precipitate (12.1.1 or 12.1.2) to a small platinum crucible, char and ignite at 700 to 800°C for approximately 30 min. Cool, add 0.5 to 1.0 g of Na<sub>2</sub>CO<sub>3</sub>, mix well with the flattened end of a glass rod, and fuse at a moderate heat for 5 to 10 min. Cool, add 10 to 15 mL of hot water, and digest until the melt has completely dissolved. Filter into a 100-mL beaker through a 7-cm medium paper and wash 4 to 5 times with cold 0.5 % Na<sub>2</sub>CO<sub>3</sub> solution. Reserve the filtrate (B).

12.3 Cover the funnel and place a 150-mL beaker under it; dissolve the carbonate precipitate with hot 5 % HCl. Rinse the platinum crucible, cover with hot 5 % HCl, and pour through the filter. Wash the paper 4 to 5 times with hot 5 % HCl. Discard the paper. Neutralize the filtrate (using methyl red as the indicator) with NH<sub>4</sub>OH, reacidify with 1 mL of HCl, and dilute to 100 mL. Heat to near boiling; add dropwise with stirring 5 mL of 10 % ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) solution or 1 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1). Digest near boiling 30 min; cool for 2 h. Filter through a 7-cm fine paper; police the beaker with a bit of paper pulp. Wash 5 to 6 times with cold water containing a few drops of H<sub>2</sub>SO<sub>4</sub>. Reserve the filtrate (C).

12.4 Transfer the paper and precipitate to a tared crucible, char carefully and ignite at 800 to 1000°C for 30 min. Cool in a desiccator and weigh as BaSO<sub>4</sub>.

12.5 *Calculation*—Calculate the percent of BaO as follows:

$$\text{BaO, \%} = \text{wt} \times 0.657 \times 100/2 \quad (2)$$

## 13. Determination of R<sub>2</sub>O<sub>3</sub> by Ammonium Hydroxide Precipitation and Estimation of Al<sub>2</sub>O<sub>3</sub>:

13.1 *Determination of R<sub>2</sub>O<sub>3</sub>*:

13.1.1 Acidify the reserved Na<sub>2</sub>CO<sub>3</sub> filtrate (B) (using methyl red and HCl) (see 12.2). Reduce the volume of all three reserved filtrates (A, B, and C) (see 12.1.1 or 12.1.2, 12.2, and 12.3) and combine them so that the total volume is about 200 mL. Adjust the acidity to about 1 % HCl with NH<sub>4</sub>OH. Add about 3 to 5 mg of copper as CuCl<sub>2</sub> (as a carrier), heat to near boiling, and precipitate by passing H<sub>2</sub>S through the solution as it cools. Filter through a 7-cm medium paper into a 400-mL beaker, and wash 4 to 5 times with 1 % HCl saturated with H<sub>2</sub>S. Discard the precipitate. Boil the solution to expel H<sub>2</sub>S, add 3 to 4 mL of saturated bromine water, and boil to expel bromine.

13.1.2 Precipitate the R<sub>2</sub>O<sub>3</sub> by adding NH<sub>4</sub>OH dropwise using methyl red indicator, add 3 or 4 drops in excess, and boil gently for 1 to 2 min. Filter through a 9-cm coarse paper into

a 600-mL beaker (it is not necessary to police the beaker). Allow the precipitate to drain and wash 3 times with hot neutral (methyl red) 2 %  $\text{NH}_4\text{Cl}$ . Reserve the filtrate (*D*).

13.1.3 Transfer the precipitate to the beaker in which it was precipitated, and add 10 mL of HCl (1 + 1). Stir the paper to a pulp and warm to dissolve the hydroxides. Dilute to 175 to 200 mL, heat to boiling, and repeat the precipitation with  $\text{NH}_4\text{OH}$  as before. Filter through an 11-cm coarse paper into a 600-ml beaker. Carefully police the beaker with a bit of filter pulp, allow the precipitate to drain, and wash 4 to 5 times with hot 2 %  $\text{NH}_4\text{Cl}$  as before. Washing and filtration may be facilitated by the aid of gentle suction and a platinum filter cone. Reserve the filtrate (*E*).

13.1.4 Transfer paper and precipitate to a clean, tared platinum crucible with lid. Partially cover the crucible with its lid but leave enough space for air to circulate during ignition. Place the crucible in a cold muffle furnace and bring the temperature to 1200°C for 30 min. Cover the crucible before removing from the furnace. Cool over a good desiccant and weigh.

13.1.5 *Calculation*—Calculate the percent of  $\text{R}_2\text{O}_3$  as follows:

$$\text{R}_2\text{O}_3, \% = \text{wt} \times 100/2 \quad (3)$$

( $\text{R}_2\text{O}_3$  includes  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , and traces of other elements not precipitated by  $\text{H}_2\text{S}$  and precipitated by  $\text{NH}_4\text{OH}$ .)

13.2 *Determination of Total of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{V}_2\text{O}_5$  with Cupferron:*

13.2.1 Add approximately 5 g of potassium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ ) to the crucible and precipitate and fuse until a clear melt is obtained. Fusion should be carried out at less than a red heat; otherwise, the pyrosulfate will decompose rapidly and some attack of the platinum will occur. When the fusion is complete, rotate the crucible so the mass solidifies on the sides of the crucible. Cover, cool, add 20 mL of water and a few drops of  $\text{H}_2\text{SO}_4$ , and digest until the melt has dissolved.

13.2.2 Transfer to a 250-mL beaker, cool, add 10 mL of  $\text{H}_2\text{SO}_4$ , dilute to 100 mL and cool in ice water to 10°C. Add 2 mL of cold 6 % solution of cupferron while stirring, add some paper pulp, and let set for 5 min with occasional stirring. Filter through a 9-cm medium paper, police the beaker with a bit of paper pulp, and wash eight times with cold 10 %  $\text{H}_2\text{SO}_4$  containing 1.5 g of cupferron per litre. Discard the filtrate, transfer the precipitate and paper to a tared crucible with cover, dry at 60°C, cautiously char, and finally ignite at 1000°C for 30 min.

13.2.3 *Calculation*—Calculate the percent of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{V}_2\text{O}_5$  as follows:

$$\text{Fe}_2\text{O}_3, \text{TiO}_2, \text{ZrO}_2, \text{V}_2\text{O}_5, \% = \text{wt} \times 100/2 \quad (4)$$

13.3 *Estimation of  $\text{Al}_2\text{O}_3$* —The percent of  $\text{R}_2\text{O}_3$ , (see 13.1) minus the percent of oxides found by the cupferron precipitation (see 13.2), is an estimation of  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  (and  $\text{Cr}_2\text{O}_3$ , if present). The percent of  $\text{Al}_2\text{O}_3$  is more closely estimated by subsequently determining  $\text{P}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  and deducting the percents found. The estimate of  $\text{Al}_2\text{O}_3$  may also be obtained by subtracting the percent of  $\text{Fe}_2\text{O}_3$ , etc., determined separately (see Sections 16-29) from the  $\text{R}_2\text{O}_3$ .

## 14. Determination of CaO

14.1 *Procedure:*

14.1.1 Slightly acidify (using HCl) the filtrates (*D* and *E*) from the  $\text{R}_2\text{O}_3$  precipitation (see 13.1), evaporate to about 100 mL each, combine the filtrates, and make to a volume of about 225 mL in a 400-mL beaker. Heat to near boiling; add  $\text{NH}_4\text{OH}$  dropwise in excess of about 6 drops. Add 20 mL of hot 10 % ammonium oxalate and then stir as the solution is brought to a gentle boil. Digest hot for 15 min, cool to room temperature, and after 30 min, filter on a 9-cm medium paper. It is not necessary to police the beaker. Wash 2 to 3 times with cold 0.1 % ammonium oxalate solution. Reserve the filtrate (*F*).

14.1.2 Dissolve the precipitate from the paper into the beaker used for the initial precipitation using hot HCl (1 + 4). Alternately wash three times each with hot water and hot HCl (1 + 4) and dilute to about 200 mL with hot water. Add 2.0 g of ammonium oxalate and several drops of methyl red indicator. Then add  $\text{NH}_4\text{OH}$  until the precipitate that is forming just dissolves, heat to near boiling, and add  $\text{NH}_4\text{OH}$  (1 + 1) dropwise (preferably from a buret), stirring until the solution is slightly ammoniacal (about 10 drops in excess). Digest near boiling for 15 min and cool to room temperature for 30 min. Filter on a 9-cm medium paper and police the beaker with a bit of paper pulp. Wash the precipitate six times with cold 0.1 % ammonium oxalate solution. Reserve the filtrate (*G*).

14.1.3 Transfer the precipitate to a tared platinum crucible with cover and finally ignite at 1100°C for 30 min. Cover the crucible before removing from the furnace. Cool over a good desiccant and weigh.

14.2 *Calculation*—Calculate the percent of CaO as follows:

$$\text{CaO}, \% = \text{wt} \times 100/2 \quad (5)$$

## 15. Determination of MgO

15.1 *Procedure:*

15.1.1 Slightly acidify the two filtrates (*F* and *G*) from the precipitation of calcium (see Section 14), evaporate to a volume of about 100 mL each, and combine. Cool and add 2 g of dibasic ammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ). Add  $\text{NH}_4\text{OH}$  slowly while vigorously stirring the solution with a policeman-tipped rod until the solution is approximately 10 % of  $\text{NH}_4\text{OH}$ . If precipitation is extremely slow, continue stirring until a precipitate forms. Allow the precipitate to settle overnight. Filter on a 9 or 11-cm fine filter (it is not necessary to police the beaker at this time). Wash 3 to 4 times with cold  $\text{NH}_4\text{OH}$  (1 + 40); discard the filtrate.

15.1.2 Dissolve the precipitate with hot HCl (1 + 9) into a beaker used for precipitation. Wash the paper three times each alternately with hot water and hot HCl (1 + 9). Rinse down the sides of the beaker with the acid wash solution. Cool, add 0.1 g of  $(\text{NH}_4)_2\text{HPO}_4$ , and dilute to 100 mL for small quantities of precipitate (less than 1 % MgO); or add 0.2 g of  $(\text{NH}_4)_2\text{HPO}_4$  and dilute to 200 mL for larger quantities. Neutralize with  $\text{NH}_4\text{OH}$  and then slightly reacidify. Add  $\text{NH}_4\text{OH}$  (1 + 1) dropwise from a buret while stirring the solution until precipitation appears complete. Add  $\text{NH}_4\text{OH}$  until the solution is 5 %. Let stand 4 h or overnight. Filter on a 9 or 11-cm fine paper, and police the beaker and stirring rod with the aid of a little paper pulp, making sure all precipitate

adhering to the beaker is removed. Wash 6 to 8 times with cold  $\text{NH}_4\text{OH}$  (1 + 40) solution; discard the filtrate.

15.1.3 Transfer the precipitate to a tared platinum crucible, place in a cold muffle furnace and raise the temperature to  $1000^\circ\text{C}$ ; ignite for 1 h. Cool in a desiccator and weigh.

NOTE 4—Manganese, if present in the glass, will be found in the magnesium precipitate and should be corrected accordingly, if greater than 0.01 %. Also, any barium, calcium, and  $\text{R}_2\text{O}_3$  escaping prior separations will be found in the precipitate. Thus, prior separations should be as complete as possible.

NOTE 5—MgO in amounts less than 0.25 % can be determined more conveniently and as accurately by atomic absorption spectroscopy (see Sections 52-59).

15.2 *Calculation*—Calculate the percent of MgO as follows:

$$\text{MgO, \%} = \text{wt} \times 0.3622 \times 100/2 \quad (6)$$

### **$\text{Fe}_2\text{O}_3$ , $\text{TiO}_2$ , and $\text{ZrO}_2$ BY PHOTOMETRY AND $\text{Al}_2\text{O}_3$ BY COMPLEXIOMETRIC TITRATION**

#### **16. General Considerations**

16.1 Instead of the classical extended analysis of the  $\text{R}_2\text{O}_3$  precipitate, direct colorimetric determinations of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  are applied. Because of the low percentages usually encountered, these methods are appropriate. Generally, commercial glasses will range from 0.02 to 0.25 % for  $\text{Fe}_2\text{O}_3$ ; from 0.02 to 0.05 % for  $\text{TiO}_2$ ; and from 0.005 to 0.05 % for  $\text{ZrO}_2$ . The complexiometric determination of  $\text{Al}_2\text{O}_3$  is accurate and entirely satisfactory as a routine procedure, and as a check on the classical gravimetric method.

16.2 To avoid the contamination that inevitably results from crushing glass in a steel mortar, clean pieces of glass must be found in an agate mortar (alumina mortars are unsatisfactory). If the pieces chosen for grinding are suspected of contamination, soak in hot HCl (1 + 1) for 10 min, rinse with distilled water, and dry.

#### **17. Reagents**

17.1 *CDTA Solution (1,2-Cyclohexylene Dinitrilo) Tetraacetic Acid*—Dissolve 7.3 g of CDTA in 200 mL of water by the slow addition of 20 % weight per volume NaOH solution with stirring. When the reagent has dissolved, adjust the pH to 7 with HCl (1 + 10) using a pH meter, dilute to 1 L, and store in a polyethylene bottle. It is usually practical to prepare 2 to 4 L at a time. One millilitre will complex approximately 1.0 mg of  $\text{Al}_2\text{O}_3$ .

17.2 *EDTA Solution (Ethylenediaminetetraacetic Acid Disodium Salt)*—Dissolve 7.3 g of EDTA in water and dilute to 1 L; store in a polyethylene bottle. One millilitre will complex approximately 1.0 mg of  $\text{Al}_2\text{O}_3$ . This solution may be used instead of a CDTA solution.

17.3 *Ethyl Alcohol, Absolute (Anhydrous)*—100 % or 200 proof reagent quality.

17.4 *Ferric Oxide Standard Solution (1 mL = 0.1 mg  $\text{Fe}_2\text{O}_3$ )*—Weigh 0.4911 g of reagent ferrous ammonium sulfate into a 1-L volumetric flask, dissolve in water, add 8 to 10 mL of HCl, dilute to volume, and mix. The fact that the iron may slowly oxidize is of no consequence as it is subsequently reduced when developing the 1,10-phenanthroline complex.

17.5 *Hydrochloric Acid, Dilute (1 + 4)*—Dilute 1 volume of HCl (approximately 37 %) with 4 volumes of water. Prepare 2 L.

17.6 *Hydroxylamine Hydrochloride (10 % weight per volume in water)*—Filter if necessary.

17.7 *Nitric Acid, Dilute (1 + 1)*—Dilute 1 volume of  $\text{HNO}_3$  (approximately 70 %) with 1 volume of water. Prepare 2 L.

17.8 *1,10-Phenanthroline Solution*—The solution may be prepared from the monohydrate or hydrochloride. The latter is readily water-soluble; the monohydrate requires heating. Dissolve 1.2 g of the monohydrate by adding to 800 mL of hot water; stir and heat until in solution, cool and dilute to 1 L; store in a dark bottle or in a dark place. If the hydrochloride is used, dissolve 1.3 g in 200 to 300 mL of water and dilute to 1 L; protect from light during storage. Five millilitres of either solution will complex 0.6 mg of  $\text{Fe}_2\text{O}_3$  (10 mL will complex 1.2 mg). This will cover a transmittance curve of from 100 % *T* to about 12 to 17 %, depending on instrumentation. The absorbance for 0.6 mg of  $\text{Fe}_2\text{O}_3$  in 100 mL volume equals approximately 0.825 in a 1-cm absorption cell.

17.9 *Pyridine, Analytical Reagent*.

17.10 *Pyrocatechol Violet*—Prepare a 0.05 % w/v solution in absolute ethyl alcohol by dissolving 12.5 mg of reagent in 25 mL of absolute alcohol. The solution must be prepared daily just before use. The reagent should be tested for sensitivity before use. Test the reagent with a known quantity of  $\text{ZrO}_2$  as described in Section 21 and if the absorbance or present transmittance indicated in 21.4 is not obtained, discard the lot of reagent and obtain a fresh lot for further use.

17.11 *Sodium Acetate (Buffer) Solution (2 M)*—Dissolve 272 g of sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) per litre of aqueous solution prepared. Filter before use if necessary. Since sodium acetate solutions tend to develop mold growth with age, a preservative can be used; 0.025 g of parachlorometaxylene per litre has been found satisfactory for this purpose.

17.12 *Thioglycolic Acid ( $\text{CH}_2\text{SHCOOH}$ , Reagent, Assay 96 to 97 %)*—Prepare a 20 % volume solution; keep refrigerated.

17.13 *Tiron Reagent (Disodium-1,2-di-Hydroxybenzene-3,5-Disulfonate)*—Prepare a 5 % weight per volume solution. Filter if necessary. The solution should be nearly colorless. Protect from light in storage.

17.14 *Titanium Dioxide, Standard Solution (1 mL = 1.0 mg  $\text{TiO}_2$ )*—Weigh 1.0026 g of NIST SRM No. 154b titanium dioxide, and prepare 1 L of solution as directed by the certificate furnished with the material for use as a standard for colorimetry. (If an older supply, Nos. 154 or 154a, is available, use the appropriate weight as determined from the certified percent of  $\text{TiO}_2$ .)

17.15 *Titanium Dioxide, Dilute Standard Solution (1 mL = 0.1 mg  $\text{TiO}_2$ )*—Pipet 50 mL of the 1.0 mg  $\text{TiO}_2$ /mL standard solution into a 500-mL volumetric flask, add 15 mL of  $\text{H}_2\text{SO}_4$ , and dilute to about 400 mL; mix by swirling. Cool to room temperature, if necessary; dilute to volume and mix.



17.16 *TOPO Reagent (tri-n-Octyl-Phosphine Oxide)*—Prepare an approximately 0.01 M solution by dissolving 1 g of reagent in 200 ml of cyclohexane.

17.17 *Xylenol Orange Tetrasodium Salt (Indicator) Solution*—Dissolve 0.5 g in 100 mL of water, and add 1 or 2 drops of HCl as stabilizer.

17.18 *Zinc Standard Solution*—Prepare from ACS reagent or spectroscopically pure metal freed of oxide surface film. Dissolve 1.283 g of metal in 30 mL of HCl (1 + 4), and dilute to 2 L with water. One millilitre of Zn solution = 0.500 mg of Al<sub>2</sub>O<sub>3</sub> and approximately 0.50 mL of CDTA or EDTA solution. Since the zinc solution is the standard for the Al<sub>2</sub>O<sub>3</sub> determination, it must be prepared with care and accuracy.

17.18.1 *Standardization of CDTA or EDTA Solution with Standard Zinc Solution*—Accurately pipet 10 or 15 mL of CDTA or EDTA solution to a 150 or 250-mL beaker and dilute to about 40 to 50 mL. Add 5 mL of 2 M sodium acetate buffer and while stirring on a magnetic stirrer, adjust the pH to 5.3 by the addition of acetic acid using a pH meter, or by using xylenol orange as a pH indicator (Note 8 in 22.3.1). Titrate with the standard zinc solution to the first perceptible color change from yellow to pinkish-red. A circle of filter paper placed under the beaker will aid in detecting the end point. Repeat at least twice more and average the titers. Millilitres of zinc solution divided by millilitres of CDTA or EDTA equals millilitres of zinc equivalent of CDTA or EDTA.

17.19 *Zirconium Oxide, Standard Solution (1 mL = 0.1 mg ZrO<sub>2</sub>)*—Standardize reagent quality zirconyl nitrate by careful ignition to the oxide as follows: accurately weigh 2.0 g of the nitrate into a tared platinum dish or crucible and gradually heat from room temperature to 1000°C. Weigh a sufficient amount of the standardized nitrate to make 1 L of solution containing 0.1 mg of ZrO<sub>2</sub>/mL. Transfer to a 1-L volumetric flask, dissolve in HNO<sub>3</sub> (1 + 1), and dilute to volume with HNO<sub>3</sub> (1 + 1).

17.20 *Zirconium Oxide, Dilute Standard Solution (1 mL = 20 µg ZrO<sub>2</sub>)*—Dilute 100 mL of the 0.1 mg ZrO<sub>2</sub>/mL standard solution to 500 mL in a volumetric flask with HNO<sub>3</sub> (1 + 1).

## 18. Procedure

18.1 Grind clean pieces of sample in an agate mortar so that the coarsest pieces would pass a 150-µm (No. 100) mesh sieve. Weigh 2.000 g of the ground sample into a 75 or 100-mL platinum dish, moisten with 5 mL of water, and, while stirring with a platinum or plastic rod, add 12 to 15 mL of HF and 12 to 15 mL of HClO<sub>4</sub>. Evaporate until fluorides begin to react, then cover with a platinum lid, allowing just sufficient space for HF to escape. When all reaction has subsided, cool, rinse the lid and sides of the dish, stir, and evaporate to strong fumes of HClO<sub>4</sub>. Cool, rinse down the sides of the dish, add 5 mL of saturated H<sub>3</sub>BO<sub>3</sub> solution, and evaporate to dryness. Eventually, partially cover the dish to remove the last traces of excess HClO<sub>4</sub>. However, do not prolong heating, as basic salts, difficult to dissolve, can result. Cool, add 10 mL of HCl (1 + 4), and digest warm until the salts are in solution (see 18.1.1 and Note 6). Transfer or filter the sample solution into a 100-mL volumetric flask; cool and dilute to volume. Prepare a

reagent blank; aliquots identical to those for the separate determinations are used as photometric references.

18.1.1 If a slight cloudiness persists at this point, it is probably a precipitate of barium sulfate (BaSO<sub>4</sub>). In this case, add a bit of paper pulp, dilute to about 35 to 40 mL, cool for about 30 min, and filter through a 5.5 or 7.0-cm fine filter into the volumetric flask. Wash moderately twice with cold water, once with 2 mL of HCl (1 + 4), and twice more with water. If a predetermined amount of sodium acetate is to be used to adjust the pH for determination of Fe<sub>2</sub>O<sub>3</sub>, the amount taken shall accommodate an aliquot taken from a sample volume containing 12 mL of HCl (1 + 4) rather than 10 mL.

NOTE 6—Sample preparation with HClO<sub>4</sub> will oxidize Cr(III) to Cr(VI); hexavalent chromium will interfere in both the determination of ZrO<sub>2</sub> and in the end point detection of the Al<sub>2</sub>O<sub>3</sub> titration. To reduce hexavalent chromium (apparent by the orange to reddish color of the perchlorate salts), transfer the solution from the platinum dish to a 150-mL beaker, dilute to 50 mL, add 7 % sulfurous acid reagent dropwise until the chromium has been reduced to Cr(III), and boil gently for about 5 min to remove excess SO<sub>2</sub>. If the solution is cloudy, proceed as in 18.1.1; otherwise, transfer directly to the volumetric flask.

18.2 *Adjustment of pH*—The procedures in this section specify adjustment of pH by the use of 2 M sodium acetate solution alone. This may be accomplished accurately by use of a pH meter. It may also be done conveniently when numerous samples are repetitiously analyzed by predetermining the quantity of 2 M sodium acetate solution required as follows: prepare a solution of 10 mL of HCl (1 + 4) diluted to 100 mL in a volumetric flask. Pipet the quantity of sample solution to be taken as specified (usually 25 mL) into a 150-mL beaker, dilute to 35 to 40 mL, and with a pH meter, record the volume of 2 M sodium acetate solution added from a buret that is required to bring the pH to 3.2 (for Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>). Add 2 mL of 20 % thioglycolic acid, 5 mL of Tiron, and then additional 2 M sodium acetate solution until the pH is 4.5; record for use in the determination of TiO<sub>2</sub>. The pH specified in the several procedures is near optimum. The use of other buffer solutions is permissible but it is recommended that their use be checked by pH measurement to determine that the specified pH is obtained.

## 19. Iron Oxide by the 1,10-Phenanthroline Method

19.1 Transfer a suitable aliquot, not to exceed an equivalent of 0.5 g (25 mL), nor containing more than 0.6 mg of Fe<sub>2</sub>O<sub>3</sub>, to a 100-mL volumetric flask. Dilute to about ¾ the volume of the flask, add 1 mL of 10 % hydroxylamine hydrochloride, 5 mL of 1,10-phenanthroline, and a predetermined amount of 2 M sodium acetate solution to adjust the pH of the solution to about 3.2. Dilute to volume and mix. When colored glasses that contain small amounts of NiO, CoO, or CuO are analyzed, use 10 mL of 1,10-phenanthroline.

19.2 After 5 min, measure absorbance or percent transmittance using 1-cm absorption cells at 508 nm on a suitable (spectro)photometer. The reagent blank is used as the reference solution.

19.3 *Calculation*—Convert the photometric reading to milligrams of Fe<sub>2</sub>O<sub>3</sub> by reference to the standard curve, and calculate the percent of Fe<sub>2</sub>O<sub>3</sub> as follows:

$$\text{Fe}_2\text{O}_3, \% = A/(B \times 10) \quad (7)$$

where:

$A$  =  $\text{Fe}_2\text{O}_3$  found in sample solution aliquot, mg, and  
 $B$  = amount of sample represented by sample solution aliquot, g

19.4 *Preparation of Standard  $\text{Fe}_2\text{O}_3$  Curve*—To a series of 100-mL volumetric flasks containing about 50 mL of water and 1 mL of HCl (1 + 4), add 0, 1, 2, 3, 4, 5, and 6 mL of standard iron solution, 1 mL of 10 % hydroxylamine hydrochloride, 5 mL of 1,10-phenanthroline, and 2 mL of 2 *M* sodium acetate solution. Dilute to volume and mix. Measure absorbance or percent transmittance as described in 19.2. Plot absorbance versus concentration on linear graph paper or percent transmittance on semi-log paper (percent transmittance on the log scale, concentration on the linear scale).

## 20. Titanium Dioxide by the Tiron Method

20.1 Transfer a suitable aliquot not to exceed 0.5 g (25 mL), nor containing more than 0.3 mg of  $\text{TiO}_2$ , to a 50-mL volumetric flask (if the aliquot taken is less than 25 mL, dilute to 25 mL before proceeding). Add in order, with mixing, 2 mL of 20 % thioglycolic acid and 5 mL of Tiron reagent solution, and adjust the pH to approximately 4.5 by the addition of a predetermined quantity of 2 *M* sodium acetate buffer solution. Dilute to volume and mix. Allow the solutions to sit 45 min before photometry to assure complete reduction of iron.

20.2 After 45 min, measure absorbance or percent transmittance in 1-cm cells at 380 nm. Compare the measurements to the standard curve and calculate the percent of  $\text{TiO}_2$  as for  $\text{Fe}_2\text{O}_3$  (see 19.3).

20.3 *Preparation of Standard  $\text{TiO}_2$  Curve*—To a series of 100 or 150-mL beakers containing 20 mL of water, pipet 0, 1, 2, and 3 mL of dilute standard  $\text{TiO}_2$  solution, and add 2 mL of 20 % thioglycolic acid and 5 mL of Tiron reagent solution. With a pH meter, adjust the pH to 4.5 by the addition of 2 *M* sodium acetate solution added from a buret. Transfer the solutions to 50-mL volumetric flasks, dilute to volume, and mix. After 15 min, measure absorbance or percent transmittance as described in 21.2. Plot the readings as described for  $\text{Fe}_2\text{O}_3$  (see 19.4). The absorbance for 0.3 mg of  $\text{TiO}_2$  in 50-mL volume is about 1.150, or a percent transmittance of 7.

## 21. Zirconium Dioxide by the Pyrocatechol Violet Method

21.1 Pipet 10 mL (0.2 g) of the sample solution to a 60-mL Squibb separatory funnel, preferably fitted with a TFE-fluorocarbon stopcock plug. Add 10 mL of  $\text{HNO}_3$ , and, if the solution has warmed significantly, cool to room temperature. Pipet 10 mL of TOPO-cyclohexane into the solution and extract zirconium by shaking or mixing for 10 min. Carefully vent the separatory funnel and then allow the liquid layers to separate. Drain off the aqueous layer and discard. Add 10 mL of  $\text{HNO}_3$ (1 + 1), shake for 2 min; allow the layers to separate, drain and reject the acid layer. Drain the TOPO-cyclohexane extract into 12-mL glass-stoppered centrifuge tubes and centrifuge for 3 to 5 min to completely separate from any aqueous phase.

21.2 Transfer with a dry pipet 5 mL of the TOPO-cyclohexane extract into a dry 25-mL volumetric flask. Add in order, while mixing, 10 mL of absolute alcohol, 1 mL of

0.05 % pyrocatechol violet, and 5 mL of pyridine from a dry pipet. Dilute to volume with absolute alcohol and mix. After 30 min, measure absorbance or percent transmittance in 1 or 5-cm cells at 655 nm. The reagent blank is the reference solution.

21.3 *Calculation*—Convert the photometric reading to micrograms of  $\text{ZrO}_2$  by means of the standard curve and calculate the percent of  $\text{ZrO}_2$  as follows:

$$\text{ZrO}_2, \% = [A/(B \times C)] \times 10^{-4} \quad (8)$$

where:

$A$  =  $\text{ZrO}_2$  found in aliquot of TOPO-cyclohexane extract,  $\mu\text{g}$ ,  
 $B$  = amount of sample represented by sample solution aliquot, g, and  
 $C$  = fraction of TOPO-cyclohexane extract.

(The equation is multiplied by  $10^{-4}$  to convert 1  $\mu\text{g/g}$  of sample to percent.)

21.3.1 *Example*—12  $\mu\text{g}$  of  $\text{ZrO}_2$  found in 5 mL of TOPO-cyclohexane extract of a 10-mL sample aliquot is calculated as follows:

$$[12/(0.2 \times 0.5)] \times 10^4 = 120 \times 10^4 = 0.012 \% \text{ ZrO}_2$$

where:

0.2 = sample in 10-mL aliquot, g, and  
0.5 = 5-mL fraction of TOPO-cyclohexane extract.

21.4 *Preparation of Standard  $\text{ZrO}_2$  Curve*—Prepare a series of solutions in 60-mL separatory funnels containing 0, 1, 2, 3, 4, and 5 mL of 20  $\mu\text{g/mL}$  standard  $\text{ZrO}_2$  solution. Dilute to 20 mL with  $\text{HNO}_3$  (1 + 1). Extract the zirconium and develop and measure the absorbance or percent transmittance of the colored complex as described in 21.1 and 21.2. The zero solution is used as the photometric reference. Plot the readings as described for  $\text{Fe}_2\text{O}_3$  in 19.4. The standard curve should be prepared so that it may be used for 1-cm and 5-cm cells. Also, since 5-mL aliquots of the TOPO-cyclohexane extracts contain but 0.5 of the  $\text{ZrO}_2$  taken, the plot will represent 10, 20, 30, 40, and 50  $\mu\text{g}$  of  $\text{ZrO}_2$ . In 1-cm cells, 50  $\mu\text{g}/25\text{-mL}$  volume should have an absorbance of approximately 0.7; in 5-cm cells, 10  $\mu\text{g}/25\text{-mL}$  volume will have the same absorbance (or about 20 % transmittance).

NOTE 7—It is advisable to carry a standard amount of  $\text{ZrO}_2$  (60 or 100  $\mu\text{g}$ ), throughout the procedure each time samples are analyzed. This serves as a check on the extraction and color-complex development. If more than 50  $\mu\text{g}$  of  $\text{ZrO}_2$  are found in the 5-mL aliquot of the TOPO-cyclohexane extract of a sample, repeat the determination using a smaller sample aliquot.

## 22. Determination of $\text{Al}_2\text{O}_3$ by CDTA or EDTA Compleximetric Titration

22.1 Transfer an aliquot equal to a 0.5-g sample (25 mL) to a 150 or 250-mL beaker. Add sufficient CDTA or EDTA to provide an approximate excess of 5 mL. Place a magnetic stir bar in the solution, stir the solution, and slowly add sufficient 2 *M* sodium acetate buffer solution to raise the pH to 3.2 to 3.5. Heat the solution to a gentle boil; the stir bar is conveniently left in the beaker. Boil for 1 min if CDTA is used, and 5 min if EDTA is used, to assure complete complexation of aluminum. Cool to room temperature, preferably in a cold-water bath.



22.2 Place the beaker on a magnetic stirrer with a circle of filter paper underneath the beaker to aid in detecting the end point. Stir the solution, add 1 or 2 drops of xylenol orange indicator, and adjust the pH to 5.3. Titrate with the standard zinc solution to the first perceptible color change from yellow to pinkish red.

22.3 *Calculation of Al<sub>2</sub>O<sub>3</sub> and Correction for Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, etc. (ZrO<sub>2</sub> and MnO<sub>2</sub>, if Determined)*—Calculate the net zinc titer by subtracting the zinc back titer from the millilitres zinc equivalent of CDTA or EDTA used. Since the zinc solution equals 0.5 mg Al<sub>2</sub>O<sub>3</sub>/mL and a 0.5-g sample is titrated, calculate the uncorrected percent of Al<sub>2</sub>O<sub>3</sub> as follows:

$$\text{Al}_2\text{O}_3, \% \text{ (uncorrected)} = \text{net zinc titer} \times 0.1 \quad (9)$$

22.3.1 *Example*—If 15 mL CDTA are added (estimated Al<sub>2</sub>O<sub>3</sub> = 2.0 %), then:

$$\begin{aligned} 15 \times 2.02 \text{ (1 mL CDTA} = 2.02 \text{ mL zinc solution)} \\ = 30.3 \text{ mL zinc equivalent CDTA} \end{aligned}$$

If zinc back titer = 8.80 mL, then

$$\begin{aligned} (30.30 - 8.80) = 21.50 \text{ mL} \\ = 2.15 \% \text{ Al}_2\text{O}_3 \text{ uncorrected} \end{aligned}$$

To correct for Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>:

$$(\% \text{ Fe}_2\text{O}_3 + \% \text{ TiO}_2) \times 0.637 = \text{equivalent \% Al}_2\text{O}_3$$

If % Fe<sub>2</sub>O<sub>3</sub> = 0.045 and % TiO<sub>2</sub> = 0.018, then:

$$(0.045 + 0.018) = 0.063 \times 0.637 = 0.040$$

$$2.15 - 0.040 = 2.11 \% \text{ Al}_2\text{O}_3 \text{ corrected for Fe}_2\text{O}_3 \text{ and TiO}_2$$

ZrO<sub>2</sub> is corrected by multiplying % ZrO<sub>2</sub> × 0.413; and % MnO × 0.719. If determined, ZrO<sub>2</sub> and MnO equivalents are added to the correction for Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and the whole subtracted from percent uncorrected Al<sub>2</sub>O<sub>3</sub>.

NOTE 8—To provide a 5-mL excess of CDTA or EDTA for complete complexation of aluminum, using a sample aliquot equal to 0.5 g, a sample containing 1.5 % Al<sub>2</sub>O<sub>3</sub> will require 12.5 mL and a sample containing 3.0 % Al<sub>2</sub>O<sub>3</sub>, 20 mL respectively. The pH of the sample solution may be adjusted to 5.3 by using a pH meter and NH<sub>4</sub>OH (1 + 1) and acetic acid; by adding a predetermined amount of 2 M sodium acetate buffer solution; or, more practically, by using xylenol orange as a pH indicator as follows: After addition of the indicator, stir the solution and add NH<sub>4</sub>OH (1 + 1) until the indicator begins to change color (pH about 5.7 to 6). Add acetic acid until the color is again a clear bright yellow. Proceed with the zinc back titration.

## Cr<sub>2</sub>O<sub>3</sub> BY VOLUMETRIC AND PHOTOMETRIC METHODS

### 23. General Considerations

23.1 Chromium is the primary colorant added to many green commercial glasses. Light-green bottle glass may contain 0.01 to 0.02 % of Cr<sub>2</sub>O<sub>3</sub>; the brilliant emerald green contains about 0.20 %. Chromium oxide may also be present as a co-colorant with other oxides (MnO, Fe<sub>2</sub>O<sub>3</sub>, NiO, CoO) to the extent of 0.005 to 0.10 %. However, its presence in colorless glasses in excess of 0.0005 % is unusual.

23.2 When Cr<sub>2</sub>O<sub>3</sub> in the sample is known or suspected to be not less than 0.05 %, the volumetric ferrous sulfate-dichromate method is used. For amounts less than 0.05 %, Cr<sub>2</sub>O<sub>3</sub> is determined photometrically by the diphenylcarbohydrazide method.

23.3 Some chromium may be present in the sample as the chromate as well as the chromic ion. To avoid loss during sample preparation or subsequent separation, all chromium is reduced to the chromic ion during sample preparation.

### 24. Determination of Cr<sub>2</sub>O<sub>3</sub> by the Ferrous Sulfate-Potassium Dichromate Method

24.1 *Reagents:*

24.1.1 *Ammonium Persulfate* ((NH<sub>4</sub>)<sub>2</sub> S<sub>2</sub>O<sub>8</sub>).

24.1.2 *Ferrous Ammonium Sulfate* (FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>·6H<sub>2</sub>O).

24.1.3 *Phosphoric Acid—Sulfuric Acid Mixture*—Add 150 mL of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 150 mL of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to 500 mL of water and dilute to 1 L. Add 0.1 N KMnO<sub>4</sub> solution dropwise until the solution is faintly pink, and heat to boiling until the permanganate is totally reduced.

24.1.4 *Potassium Dichromate Solution (0.02 N)*—Dissolve 0.9806 g of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), primary standard reagent in water and dilute to 1 L in a volumetric flask.

24.1.5 *Potassium Permanganate Solution (0.1 N (approximate))*—Dissolve 3.2 g of potassium permanganate (KMnO<sub>4</sub>) in water and dilute to 1 L.

24.1.6 *Silver Nitrate Solution (2.5 g/100 mL)*—Dissolve 2.5 g of silver nitrate (AgNO<sub>3</sub>) in 100 mL of water.

24.1.7 *Sodium Chloride Solution (20 g/100 mL)*—Dissolve 20 g of sodium chloride (NaCl) in 100 mL of water.

24.1.8 *Sodium Diphenylamine Sulfonate Indicator Solution*—Dissolve 0.160 g of sodium diphenylamine sulfonate (C<sub>6</sub>H<sub>5</sub>NHC<sub>6</sub>H<sub>4</sub>-4-SO<sub>3</sub>Na) in 250 mL of water.

24.2 *Procedure:*

24.2.1 Weigh 2.000 g of sample into a 75 or 100-mL platinum dish, moisten with 5 mL of water, and, while stirring with a platinum or plastic rod, add 12 to 15 mL of HF, 12 mL of HClO<sub>4</sub>, and 10 drops of 7 % H<sub>2</sub>SO<sub>3</sub>. Evaporate until fluorides begin to react, then cover with a platinum lid, allowing just sufficient space for HF to escape. When the reaction has subsided, cool, rinse the lid and sides of the dish, and evaporate to very light fumes of HClO<sub>4</sub>. Add 5 mL of 5 % H<sub>3</sub>BO<sub>3</sub> and again evaporate to light fuming.

NOTE 9—It is absolutely essential that at no time during sample preparation perchloric acid is allowed to heat to the point at which chromium will be oxidized to the chromate ion. This is evident if the sample solution should change to an orangish color. If this occurs, some chromyl chloride will be formed and lost by volatilization. Absolute expulsion of fluoride is not essential, and since boric acid will complex traces left in the sample solution, very light fuming of HClO<sub>4</sub> will suffice.

24.2.2 Cool the sample, transfer to a 400-mL beaker, and dilute to 200 mL. Add 2 to 3 glass beads or boiling stones and 10 drops of 0.1 N KMnO<sub>4</sub> solution, cover, and heat to boiling. Remove the beaker from the source of heat until boiling subsides. Add 1 mL of AgNO<sub>3</sub> solution and 3 g of ammonium persulfate. Keep the beaker covered to avoid mechanical loss. Boil for 10 to 12 min. (The solution should develop a rose-red color from oxidation of manganese.) Add 10 mL of NaCl solution and boil an additional 10 to 12 min to reduce permanganate and precipitate silver. Remove and cool to room temperature.

24.2.3 Add 10 mL of H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> mixture and 0.1000 g of ferrous ammonium sulfate and stir gently to dissolve. Add 1

mL of indicator and titrate the excess ferrous iron with standard dichromate until the purple-blue color is permanent for ½ to 1 min. Record as  $V_2$ . Weigh 0.1000 g of ferrous ammonium sulfate and add to 200 mL of solution containing 10 mL of  $\text{HClO}_4$  and 10 mL of  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{SO}_4$  mixture. Titrate as before and record as  $V_1$ .

24.2.4 *Calculation*—Calculate the percent of  $\text{Cr}_2\text{O}_3$  as follows:

$$\text{Cr}_2\text{O}_3\% = (V_1 - V_2) \times 0.05068/2 \quad (10)$$

## 25. Determination of $\text{Cr}_2\text{O}_3$ by the Diphenylcarbohydrazide Method

### 25.1 General Considerations:

25.1.1 The maximum amount of  $\text{Cr}_2\text{O}_3$  that may be determined by the described procedure is about 70  $\mu\text{g}$  in a 50-mL volume. If the known or suspected amount is larger than 0.007 %, take an aliquot of the prepared sample not exceeding 70  $\mu\text{g}$  for photometry. If the amount is known or suspected to be less than 0.0005 %, prepare a 2-g sample.

25.1.2 Platinum and glassware must be totally free of surface contamination. Fusion with potassium bisulfate will clean platinum, and boiling glass vessels with concentrated HCl should remove chromium from glass surfaces.

### 25.2 Reagents:

25.2.1 *Chromate Standard Solution* (1 mL = 0.1 mg  $\text{Cr}_2\text{O}_3$ )—Weigh 0.1936 g of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) into a 1-L flask, dissolve, and dilute to volume. Prepare fresh as needed from this solution, standard solutions containing 10  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3/\text{mL}$  and 1  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3/\text{mL}$ .

25.2.2 *1,5-Diphenylcarbohydrazide Solution* (0.25 % weight per volume)—Dissolve 1 g of reagent in 400 mL of acetone. Store in a glass-stoppered bottle in a cool dark place (preferably a refrigerator). This reagent is reasonably stable. However, it is advisable to test it with standard chromate solution (10 or 20  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3$ ) every 3 to 4 weeks.

25.2.3 *Polyphosphate Solution* (approximately 10 % weight per volume for complexing iron)—Weigh  $6.04 \pm 0.02$  g of sodium phosphate, dibasic ( $\text{Na}_2\text{HPO}_4$ ) and  $5.87 \pm 0.02$  g of sodium phosphate, monobasic ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ) into a 100 or 125-mL platinum dish. (If a dish this large is not available, a smaller charge should be prepared.) Mix well and fuse by slowly raising the heat of a gas burner until the melt is cherry red and only a few bubbles remain. Remove the dish from the burner (with platinum-tipped tongs) and rotate the melt to thin out the liquid layer. When the melt has lost all color from heat, plunge the dish halfway into a pan of cold water. The resulting mass should be transparent or only slightly opalescent. When cool, dissolve in 100 mL of cold water and store.

25.2.4 *Potassium Permanganate Solution* (1 %)—Prepare an approximate 1.0 % solution (0.3 N) weight per volume in water.

25.2.5 *Sodium Azide Solution* (1 %)—Prepare a 1.0 % solution weight per volume in water.

25.2.6 *Sulfuric Acid* (3 M)—Add 84 mL of  $\text{H}_2\text{SO}_4$  (approximately 98 %) to 350 mL of water, cool, dilute to 500 mL in a volumetric flask, and store in a glass-stoppered bottle.

25.2.7 *Sulfuric Acid* (3 M), treated to remove reducing substances. This solution is to be used for preparing the standard curves. Prepare the dilute acid as described in 25.2.6, except before diluting to volume, add 1 %  $\text{KMnO}_4$  solution dropwise until the solution is just pink. Heat until all the permanganate has been reduced. Cool, dilute to volume, and store in a glass-stoppered bottle.

### 25.3 Procedure:

25.3.1 Weigh 1.000 or 2.000 g of sample into a 75 or 100-mL platinum dish and prepare the sample with  $\text{H}_2\text{SO}_4$  as described in 12.1. Add 20 mL of HCl (1 + 1) to the dry residue, and digest to dissolve the sulfates (disregard the presence of any barium sulfate if present). Transfer to a 250-mL beaker, dilute to 150 mL, heat to boiling, and precipitate  $\text{R}_2\text{O}_3$  with  $\text{NH}_4\text{OH}$  (methyl red), adding 4 to 5 drops in excess. Boil gently for 2 min and filter through a 9-cm coarse filter paper; do not police the beaker. Wash 3 to 4 times with hot neutral 2 %  $\text{NH}_4\text{Cl}$  solution. Discard the filtrate. Transfer the paper and precipitate to the beaker used for precipitation, add 10 mL of HCl (1 + 1) and macerate the paper. Add 10 mL of water, cover the beaker, and digest hot for about 5 min. Filter through a 9-cm medium paper into a 100-mL beaker or 100-mL volumetric flask if an aliquot is to be taken. Wash 4 times with hot water; allow the pulp to drain well between washes.

25.3.2 Add 2 mL of 3 M  $\text{H}_2\text{SO}_4$  to the sample solution (or aliquot containing less than 70  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3$  in a 100-mL beaker) and evaporate to just perceptible fuming of  $\text{H}_2\text{SO}_4$ . If the solution is colored from traces of organic matter, cautiously add 5 to 10 drops of  $\text{HNO}_3$  and again evaporate to light fuming of  $\text{H}_2\text{SO}_4$ . Cool, rinse down the sides of the beaker and again evaporate to just perceptible fumes to completely expel HCl.

25.3.3 Prepare a reagent blank for photometric reference, except omit the precipitation step with  $\text{NH}_4\text{OH}$  (25.3.1). (If platinum and glassware are clean, the reagent blank should not exceed 1  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3$ .)

25.3.4 Add 20 mL of water, 2 to 3 glass beads or boiling stones, and 5 drops of 1 %  $\text{KMnO}_4$  solution, cover, and heat the solution to boiling. Maintain at a gentle boil for 20 min; if necessary, add additional  $\text{KMnO}_4$  solution to maintain an excess, and hot water to maintain the volume. Cool slightly, add sodium azide solution 1 drop at a time, and stir for 20 s between drops until the excess  $\text{KMnO}_4$  is reduced. Cool immediately in a cool water bath. Add 1 mL of polyphosphate solution and transfer the solution to a 50-mL volumetric flask. Dilute to 40 mL. Add 2 mL of diphenylcarbohydrazide solution, dilute to 50 mL, and mix.

25.3.5 After 10 min, measure absorbance or percent transmittance at 540 nm in 5-cm cells for quantities of 15  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3$  or less, or in 1-cm cells for quantities more than 15  $\mu\text{g}$ .

25.3.6 *Calculation*—Convert the photometric measurement to micrograms of  $\text{Cr}_2\text{O}_3$  by reference to the appropriate standard curve and calculate percent of  $\text{Cr}_2\text{O}_3$  as follows:

$$\text{Cr}_2\text{O}_3, \% = (A/B) \times 10^{-4} \quad (11)$$

where:

A =  $\text{Cr}_2\text{O}_3$  found in sample solution,  $\mu\text{g}$ , and

$B$  = amount of sample represented by the sample solution (or aliquot), g.

(The equation is multiplied by  $10^{-4}$  to convert  $1 \mu\text{g/g}$  of sample to percent.)

**25.3.7 Preparation of the Standard Curves**—To a series of 50-mL volumetric flasks containing about 20 mL of water, add 2 mL of the permanganate-treated 3  $M$  sulfuric acid, 1 mL of polyphosphate solution, and 0, 2, 5, 10, and 15 mL of the 1  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3/\text{mL}$  standard chromate solution. Add 2 mL of diphenylcarbohydrazide mix, dilute to volume, and mix. After 10 min, measure absorbance or percent transmittance in 5-cm cells at 540 nm; the zero solution is used as the photometric reference. Prepare another series of flasks as above and add 0, 1, 2, 5, and 7 mL of the 10  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3/\text{mL}$  standard chromate solution. Develop the colored complex and make photometric measurements as for the first series but use 1-cm cells. Plot the photometric readings as described for  $\text{Fe}_2\text{O}_3$ . The first curve represents  $\text{Cr}_2\text{O}_3$  in concentrations of 0 to 15  $\mu\text{g}/50 \text{ mL}$  in 5-cm cells; the second 0 to 70  $\mu\text{g}/50 \text{ mL}$  in 1-cm cells.

## MnO BY THE PERIODATE OXIDATION METHOD

### 26. General Considerations

**26.1 Manganese as MnO** is found in most soda-lime glasses, usually in amounts of 0.001 % to 0.1 %. Only a few specially colored glasses may exceed 0.1 %. Only chromium and large amounts of iron are likely interferences. In the absence of chromium (less than 0.01 %), the absorbance of the colored solution is measured at 525 nm. If  $\text{Cr}_2\text{O}_3$  exceeds this amount, the measurement is made at 545 nm; the absorbance at 545 nm is less than at 525 nm but still satisfactory for photometry. The interference of iron is not serious. If the  $\text{Fe}_2\text{O}_3$  in the sample exceeds 0.50 %, the slight absorbance of iron can be compensated for by adding a comparable quantity to the reagent blank.

### 27. Reagents

**27.1 Manganese, Standard Solution: (Stock Solution) (1 mL = approximately 1 mg MnO)**—Accurately weigh and dissolve approximately 0.775 g of pure manganese metal in 10 to 15 mL of  $\text{HNO}_3$  by heating. When the metal has dissolved, dilute to about 50 mL and boil to remove oxides of nitrogen. Cool and dilute to 1 L ( $\text{Mn} \times 1.2912 = \text{MnO}$ ).

**27.2 Manganese, Dilute Standard Solution A (1 mL = 0.1 mg MnO)**—Dilute an approximate amount of stock solution (27.1) to 1 L to equal 0.1 mg/mL.

**27.3 Manganese, Dilute Standard Solution B (1 mL = 0.01 mg MnO)**—Dilute 100 mL of dilute standard manganese solution A to 1 L.

**27.4 Potassium Periodate ( $\text{KIO}_4$ ).**

### 28. Procedure

**28.1** Weigh 1 g of glass into a 50 to 75-mL platinum dish; add 2 mL of water, 5 to 6 mL of HF, 5 to 6 mL of  $\text{HClO}_4$ , and proceed as described in 12.1.1. Evaporate to near dryness, but remove from the source of heat while the salts are still moist. Dissolve the residue in 10 mL of  $\text{HNO}_3$  and 10 mL of water. Transfer the sample solution to a 100 or 150-mL beaker and dilute to 40 mL. Add 1 mL of  $\text{H}_3\text{PO}_4$ , 2 to 3 glass beads or boiling chips, and 0.3 g of  $\text{KIO}_4$ . Cover the beaker and heat to

boiling. Boil gently for 20 min. Cool, transfer to a 50-mL volumetric flask, and dilute to volume with water free of reducing substances.

**NOTE 10**—Some water (particularly deionized water) may contain reducing substances. If such is the case, add 10 mL of  $\text{HNO}_3$  and 1 g of  $\text{KIO}_4$  to 400 mL of water in a boiling flask and boil for about 5 min. Cool before use. Double distilled water may be used, if available, and is preferred.

**28.2** Prepare a reagent blank, carrying it throughout the procedure, and use it as the photometric reference solution.

**28.3** Measure absorbance or percent transmission at 525 nm in the absence of chromium, or at 575 nm if chromium is present. Compare to the appropriate standard curve. For quantities of 0.01 % MnO or less, measurement is made in 5-cm absorption cells; for quantities exceeding 0.01 %, measurement is made in 1-cm cells.

**NOTE 11**—In a volume of 50 mL, and with 1-cm absorption cells, 1.5 mg of MnO will give an absorbance of about 0.950. If the absorbance is greater than this, an appropriate aliquot may be taken and diluted with water (Note 10), and the absorbance of the aliquot measured. Conversely, a smaller sample may be taken and the analysis repeated.

**28.4 Calculation**—Calculate the percent of MnO as follows:

$$\text{MnO, \%} = \frac{\text{mg MnO}}{\text{wt of sample}} \times 0.1 \quad (12)$$

### 29. Preparation of Standard Curve(s)

**29.1 For 0.000 to 0.01 % MnO:**

**29.1.1** To a series of 100 or 150-mL beakers, add 0, 2, 4, 6, 8, and 10 mL of dilute standard solution B (1 mL = 0.01 mg MnO). Add 10 mL of  $\text{HNO}_3$ , 1 mL of  $\text{H}_3\text{PO}_4$ , and dilute to 40 mL. Add 0.3 g of  $\text{KIO}_4$ , and proceed as in 28.1.

**29.1.2** Measure the MnO at 525 and 545 nm in 5-cm absorption cells. Plot both curves on the same graph sheet. Absorbance is plotted on linear graph paper and percent transmittance on semi-log paper. The 0.000 % Mn solution is used as the photometric reference.

**29.2 For 0.01 to 0.15 % MnO**—To a series of 100 or 150-mL beakers, add 0, 1, 2, 5, 10, and 15 mL of dilute standard solution A (1 mL = 0.1 mg MnO). Proceed as described in 29.1, except use 1-cm absorption cells for the photometric measurements.

## $\text{Na}_2\text{O}$ BY THE ZINC URANYL ACETATE METHOD AND $\text{K}_2\text{O}$ BY THE TETRAPHENYLBORATE METHOD

### 30. Reagents

**30.1 Alcoholic Wash Solution, Acidified**—Transfer 400 mL of 95 % ethyl alcohol to a 500-mL glass-stoppered bottle or flask, add 4 mL of acetic acid and about 2 g of sodium zinc uranyl acetate precipitate. Place on a magnetic stirrer and stir for 15 min. For use, filter through a Büchner-type medium-porosity glass filter. The filtered solution is stable for several days to a week if stored in the dark. Solution kept over the precipitate is somewhat more stable. If a precipitate appears on the walls of the container, discard the solution and prepare fresh. Reagent alcohol (95 parts 3A alcohol, 5 parts isopropyl



alcohol, volume per volume) is suitable. However, if it is labeled “absolute” or “anhydrous” before preparation, add 5 mL of water to each 95 mL of the absolute reagent alcohol to be used.

**30.2 Potassium Wash Solution**—Prepare a water-saturated solution of potassium tetraphenylboron as follows: Add 40 to 50 mg of KCl to a 150-mL beaker and dilute to 50 mL. Add 2 mL of HCl and cool to 5°C in an ice bath. Precipitate and filter as described in 33.1, and wash three to four times with water. Transfer the precipitate to a 500-mL glass-stoppered bottle or flask; fill nearly full with water and stir for 15 min. Filter through a fine-porosity glass filter before use. The wash solution is used at room temperature, and is stable for at least 3 months when stored over the precipitate.

**30.3 Sodium Tetraphenylboron Solution (1 %)**—Dissolve 5 g of sodium tetraphenylboron reagent ( $\text{NaB}(\text{C}_6\text{H}_5)_4$ ) in 500 mL of water (the solution probably will not be absolutely clear). Add 10 to 20 mg of aluminum chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) and dissolve. Add 1 mL of 0.1 % phenolphthalein indicator and, dropwise, 1 N NaOH solution until the solution is just pink. Allow the solution to set 10 to 15 min and filter through a large, coarse filter paper. The slightly alkaline solution is stored in a polyethylene bottle, and, if refrigerated, is stable for at least 3 months.

**30.4 Zinc Uranyl Acetate Reagent**—For approximately 2 L of solution weigh 200 g of uranyl acetate ( $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ) and 554 g of zinc acetate ( $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ) into a 3- or 4-L beaker or flask. Add 1746 mL of water and 54 mL of acetic acid. Stir and heat until the solution is clear or nearly so (usually when the temperature has reached about 70°C). A magnetic stirrer-hot plate is convenient for this purpose. When solution is complete, cool to room temperature, preferably 22 to 23°C. Then, while stirring the solution, add 2 g of sodium zinc uranyl acetate precipitate dissolved in 20 mL of hot water containing a few drops of acetic acid. If precipitate is not available, 20 mL of a solution containing 5 to 10 mg of NaCl can be used instead. Stir for 1 h and transfer to a polyethylene bottle. The solution may be filtered and used without further aging. Filter through a medium-porosity glass filter and store in a polyethylene bottle (a 150-mL Büchner-type funnel is convenient). Filtered solution, if kept at room temperature, need not be returned to the bottle containing precipitate.

### 31. Preparation of Sample

**31.1** Weigh 1 g of sample into a 50- or 75-mL platinum dish, moisten with 1 to 2 mL of water, and add 5 to 6 mL of HF and 6 to 7 mL of  $\text{HClO}_4$ . Proceed as described under determination of BaO (12.1.1). When the salts are dry, dissolve in 15 mL of hot water and 4 mL of HCl; transfer to a 100-mL volumetric flask. If a cloudiness persists in the dissolved sample, it is most probably due to barium sulfate. In this case, add a bit of paper pulp and filter through a 7-cm fine paper into the flask. Wash with hot water. Cool the solution to room temperature and make to volume.

### 32. Determination of $\text{Na}_2\text{O}$

**32.1** Accurately transfer a 5-mL (0.05-g) aliquot for samples containing more than 8 %  $\text{Na}_2\text{O}$  or a 10-mL (0.10-g) aliquot for less than 8 %  $\text{Na}_2\text{O}$  into a 50-mL platinum dish.

Add 5 to 6 drops of  $\text{HClO}_4$  and evaporate to dryness. Cool, dissolve the residue with exactly 1 mL of water, and add 10 mL of zinc uranyl acetate reagent; additions should be made with a pipet. Stir the sample for 12 to 15 min with a slow-speed stirrer (about 350 rpm).

**32.2** Filter through a tared medium-porosity fritted-glass or porcelain filtering crucible. Transfer the precipitate with the aid of a policeman and the zinc uranyl acetate reagent as wash solution. When all the precipitate is transferred, wash three to four times with 2-mL portions of the reagent, four to five times with the alcohol wash solution, and two times with 2-mL portions of ether. Allow the crucible to remain over the filtering flask for 1 min. Wipe the outside of the crucible with a piece of damp chamois, place in a desiccator for 30 min, and weigh.

**NOTE 12**—Adequate stirring is essential to complete precipitation of sodium. This can be accomplished by using rods with a proper configuration. For use with 50-mL semiround platinum dishes, a 4-mm diameter rod 90 to 95 mm long, bent about 30 mm from one end and at an angle of 12 mm from the vertical, has been found adequate. The precipitate must be well suspended during stirring. A small “pile-up” directly under the stirrer is usually not detrimental, but if precipitate remains along the periphery of the bottom of the dish, stirring can be considered as inadequate. The speed of the stirrer should be adjusted to about 350 rpm.

**32.3 Calculation**—Calculate the percent of  $\text{Na}_2\text{O}$  as follows:

$$\% \text{Na}_2\text{O for 0.05 g aliquot} = \text{wt} \times 0.403 \times 100 \quad (13)$$

$$\% \text{Na}_2\text{O for 0.10 g aliquot} = \text{wt} \times 0.2015 \times 100 \quad (14)$$

### 33. Determination of $\text{K}_2\text{O}$

**33.1** Transfer a 50-mL aliquot (0.50 g) sample to a 150-mL beaker (if the expected potassium is more than 2.5 %  $\text{K}_2\text{O}$ , take an aliquot equivalent to 0.2 g, add HCl to equal 2 mL, and dilute to 50 mL). Place in an ice-water bath and cool to 5°C. Add 25 mL of sodium tetraphenylboron reagent also cooled to 5°C. Mix and allow to set in the cold bath for 10 min. Filter on a tared fine-porosity fritted-glass or porcelain filtering crucible. Police the beaker carefully and wash the precipitate three to four times with 5-mL portions of the wash solution. Since the wash solution is saturated with the potassium salt, it is used at room temperature. Dry at 110 to 120°C for 1 h, cool, and weigh.

**33.2 Calculation**—Calculate the percent of  $\text{K}_2\text{O}$  as follows:

$$\text{K}_2\text{O, \%} = \text{wt} \times (0.13145 \times 100) / \text{sample wt} \quad (15)$$

### $\text{SO}_3$ (TOTAL SULFUR)

### 34. General Considerations

**34.1** The determination of sulfur trioxide ( $\text{SO}_3$ ) presupposes that all sulfur present in the sample is present as the sulfate ion. This condition usually holds for “flint” and “green” glasses. However, “amber” or brown glasses usually contain sulfide ion and ordinary sample preparation will entail loss of sulfur as hydrogen sulfide. Provision must be made, therefore, to have a suitable oxidant present during dissolution of the glass. When the sample contains sulfide sulfur (S), an estimation of sulfate sulfur is obtained by determining S and correcting the total sulfur as  $\text{SO}_3$  for the amount found. A second consideration is that the initial precipitation of  $\text{BaSO}_4$  is usually too impure for accurate analysis without purification and reprecipitation.

### 35. Procedure

35.1 Weigh 3 g of sample into a 125-mL platinum dish, moisten with 5 mL of water, add 5 mL of HNO<sub>3</sub> (1 + 1) saturated with bromine, and then slowly, stirring with a platinum rod, add 15 to 20 mL of HF. If the sample is a sulfide-amber glass, place the dish in a shallow pan of cold water before adding the HF so that the sample decomposes slowly. After 5 min, proceed with the evaporation. Evaporate to dryness. Cool, cover with a platinum lid, and add 15 mL of HClO<sub>4</sub>; heat to gentle fuming, keeping the dish nearly covered to allow only sufficient space for HF to escape. When all reaction has subsided, cool, rinse the cover and sides of the dish with hot water, mix, and evaporate to strong fumes. Cool, add 5 mL of saturated H<sub>3</sub>BO<sub>3</sub>, and evaporate until most of the acid has been expelled, occasionally stirring to break crusts of salt.

35.2 Cool, add 30 mL of warm water and 1 mL of HCl, digest for a few minutes, and transfer to a 250-mL beaker. If barium is present, the solution will contain some BaSO<sub>4</sub>, in which case, carefully police the platinum dish with a bit of paper pulp and transfer to the sample solution. Dilute the solution to 150 mL, heat to boiling, and slowly add 10 mL of 10 % BaCl<sub>2</sub> solution. Digest covered for 30 min and cool for 2 h or overnight. Filter the precipitate on a 7 or 9-cm fine filter paper, carefully transferring all of the precipitate to the filter with the aid of a bit of paper pulp. Wash 3 to 4 times with cold water; discard the filtrate.

35.3 Transfer the paper to a platinum crucible, char, and ignite at about 700 to 800°C for 30 min. Cool, add 1 g of Na<sub>2</sub>CO<sub>3</sub>, mix the precipitate and Na<sub>2</sub>CO<sub>3</sub> with the flattened end of a glass rod, carefully brush adhering particles into the crucible, and fuse at a moderate heat for 5 to 10 min. Cool, add 20 mL of hot water, and digest hot until the melt has completely disintegrated. Filter through a 7-cm medium paper into a 150-mL beaker, and wash four to five times with cold 0.5 % Na<sub>2</sub>CO<sub>3</sub>. Discard the paper and precipitate.

35.4 Cover the beaker, add methyl red indicator and then HCl dropwise with stirring until the solution is acid; add 0.5 mL in excess, dilute to 100 mL, and heat to boiling to remove CO<sub>2</sub>. Slowly add 2 to 3 mL of 10 % BaCl<sub>2</sub> solution with stirring and digest hot for 30 min (keep the beaker covered as much as possible during all these operations). Cool for 2 h and filter on a 7-cm fine paper. Carefully police the beaker with a bit of paper pulp, and wash the precipitate 6 times with cold water. Ignite in a tared crucible at 800 to 900°C for 30 min. Cool in a desiccator and weigh.

35.5 *Calculation*—Calculate the percent of SO<sub>3</sub> as follows:

$$\text{SO}_3, \% = \text{wt} \times 0.343 \times 100/3 \quad (16)$$

### As<sub>2</sub>O<sub>3</sub> BY VOLUMETRIC METHOD

### 36. General Considerations

36.1 The amount of arsenic in most commercial soda-lime glasses generally does not exceed 0.05 %, although some glasses may contain considerably more. Also, it exists in the glass in two valences: the trioxide and the pentoxide. Preparation of the sample must ensure oxidation to the pentavalent form to avoid loss of trivalent arsenic. If a differentiation between the two oxidation states is required, a second sample

is prepared, omitting oxidation of trivalent arsenic, and a determination of pentavalent arsenic only is obtained. The difference between total and pentavalent arsenic represents trivalent arsenic.

### 37. Apparatus

37.1 *Distillation Apparatus*—Apparatus No. 3 (see Section 12 of Practices E 50).

37.2 *Potentiometric Apparatus*—Any suitable pH meter operated to read millivolts.

37.3 *Semimicro Buret* capable of delivery and reading of 0.01-mL increments.

### 38. Reagents

38.1 *Arsenic Trioxide, Standard Solution (1 mL = 1 mg As<sub>2</sub>O<sub>3</sub>)* Dissolve 1.0000 g of primary standard arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) in 20 mL of 1 N sodium hydroxide (NaOH) solution. Dilute to 200 mL, acidify with HCl, add 1 mL in excess, and dilute to 1 L in a volumetric flask.

38.2 *Potassium Bromate Solution (0.02 N)*—Dry crushed crystals of potassium bromate (KBrO<sub>3</sub>) for 1 h at 110°C. Dissolve 0.5567 g in water and dilute to 1 L. Standardize as described in Section 40.

### 39. Procedure

39.1 Weigh 2.000 g of sample into a 75 or 100-mL dish. Moisten with 5 mL of water, add while stirring 12 to 15 mL of HClO<sub>4</sub>, 5 mL of HNO<sub>3</sub>, 5 drops of 0.1 N KMnO<sub>4</sub> solution and 10 to 12 mL of HF. When the sample has decomposed, add a few more drops of KMnO<sub>4</sub> solution, if necessary, and proceed with the evaporation as described in 12.1.1. In the final expulsion of HClO<sub>4</sub>, do not evaporate to dryness, but leave about 2 to 3 mL of acid remaining in the sample.

39.2 Cool, add 5 mL of water, and transfer to the distillation apparatus with 15 to 20 mL of concentrated HCl. Add 0.5 g of hydrazine dihydrochloride dissolved in 5 mL of HCl, and 2 to 3 mL of HBr. Dilute with HCl to a volume of 50 mL. (Mark the flask so this can be readily ascertained.) Add 50 mL of water to a 400-mL beaker to receive the distillate. Place the receiver in a pan of ice water or cold bath of running water. Adjust the apparatus so that the tip of the condenser dips into the receiving solution about ¼ to ½ in. (6 to 12 mm). Start a slow stream of CO<sub>2</sub> (5 to 10 bubbles per second) through the apparatus. Distill at a moderate rate until the temperature reaches 111°C. Add 50 mL of HCl to the dropping funnel of the apparatus and then add dropwise to the distillation flask, maintaining a temperature of 111°C. When all the acid has been added, discontinue the distillation. Remove the beaker containing the distillate from under the condenser and wash off the condenser tip with water.

39.3 Dilute the distillate to 300 mL and cool to room temperature if necessary. Titrate potentiometrically, using a platinum-calomel electrode pair, with 0.02 N KBrO<sub>3</sub> solution and a semimicro buret.

39.4 *Calculation*—Calculate the percent of As<sub>2</sub>O<sub>3</sub> as follows:

$$\text{As}_2\text{O}_3, \% = \text{ml} \times 0.0009891/\text{sample wt} \times 100 \quad (17)$$

#### 40. Standardization of 0.02 N Potassium Bromate Solution

40.1 Before titration of the sample, standardize the 0.02 N  $\text{KBrO}_3$  solution against the arsenite standard. This serves not only as a check on the normality of the  $\text{KBrO}_3$  solution but also, and as importantly, on the proper functioning of the potentiometric apparatus and electrodes.

40.2 To 300 mL of  $\text{HCl}$  (1 + 3) in a 400-mL beaker, pipet 5 mL of standard arsenite solution (1 mL = 1 mg  $\text{As}_2\text{O}_3$ ). Titrate potentiometrically, using a platinum-calomel electrode pair, with 0.02 N  $\text{KBrO}_3$  solution and a semimicro buret. The potential change is 300 mV or more, and quite steep; 5 mg of  $\text{As}_2\text{O}_3$  = 5.06 mL of 0.02 N  $\text{KBrO}_3$  solution.

### PROCEDURES FOR ROUTINE ANALYSIS

#### 41. General Considerations

41.1 These procedures are designed for rapid, routine analysis. They are capable of producing results of satisfactory precision and accuracy. However, the proviso that “the analyst should check his procedures by the use of reference standards” is advised. Silica ( $\text{SiO}_2$ ) is determined by a single dehydration method, with a colorimetric recovery of soluble silica. Two general schemes for the remaining major oxides in the glass are described: (1) the determination of  $\text{BaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  gravimetrically; and  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$  by compleximetric titration; and (2) the determination of  $\text{Al}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{CaO}$ , and  $\text{MgO}$  by atomic absorption, and  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  by flame emission spectrophotometry. A combination of these two schemes may be practical depending upon time and instrumentation available.

41.2 A separate sample is prescribed for the determination of  $\text{BaO}$  gravimetrically. This is necessary because sulfate interferes with the gravimetric determination of  $\text{Na}_2\text{O}$ , and ammonium (if used) with the determination of  $\text{K}_2\text{O}$ . Also, by use of a separate sample for  $\text{BaO}$ , the determination of the other constituents can proceed without waiting for  $\text{BaO}$  to be separated. Obviously, when  $\text{BaO}$  is known to be absent, no sample preparation is necessary.

#### SILICA BY THE SINGLE DEHYDRATION METHOD

##### 42. Reagents

42.1 *Ammonium Molybdate Solution* (0.3 M Molybdate)—Dissolve 26.5 g of ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) in 400 mL of water. Adjust pH to 7.0 with 6 N  $\text{NaOH}$  solution, using a pH meter. Dilute to volume in a 500-mL volumetric flask and store in a polyethylene bottle. A sodium molybdate solution of equal strength and pH also is satisfactory.

42.2 *Silicon Dioxide Standard Solution* (1 mL = 0.1 mg  $\text{SiO}_2$ )—Fuse 0.1000 g of pure anhydrous silicon dioxide ( $\text{SiO}_2$ ) with 1 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in a covered platinum crucible or dish. Cool, dissolve completely in water, dilute to 1 L in a volumetric flask, and store immediately in a polyethylene bottle. It is recommended that pure quartz (99.9 % +) be used for preparation of the standard. Grind in an agate mortar to pass a 150- $\mu\text{m}$  (No. 100) sieve and ignite at 1000 to 1200°C for 1 h. Store in a desiccator.

##### 43. Procedure

43.1 Weigh 0.5000 g of powdered sample and 1.0 g of  $\text{Na}_2\text{CO}_3$  into a 75-mL platinum dish (or alternatively, 1.000 g

of sample and 1.5 to 2 g of  $\text{Na}_2\text{CO}_3$ ) and proceed with fusion, dehydration, and filtration as described in 10.1 and 10.2. However, catch the filtrate from the first dehydration in a 200-mL volumetric flask and reserve for the molybdate photometric recovery. Transfer the precipitate to the dish used for fusion and dehydration and determine weight of silica as described in 10.4. The weight of  $\text{SiO}_2$  recovered by dehydration,  $A = W_1 - W_2$ .

43.2 Cool the filtrate to room temperature, dilute to volume, and mix. Transfer a 20-mL aliquot to a 50-mL volumetric flask and dilute to 30 to 35 mL. Add 10 mL of ammonium molybdate solution from a pipet, gently swirling the solution, dilute to volume, and mix. After 2 min, measure absorption or percent transmittance in 1-cm cells at 400 nm. Determine weight of  $\text{SiO}_2$  recovered,  $B$ , by reference to the standard curve.

$$\text{Weight of SiO}_2 \text{ in grams} = \text{mg}/0.1 \times 10^{-3}$$

43.3 *Calculation*—Calculate the percent of  $\text{SiO}_2$  as follows:

$$\text{SiO}_2, \% = [(A + B) \text{ wt of sample}] \times 100 \quad (18)$$

##### 44. Preparation of Standard Curve

44.1 Transfer 1.0, 2.0, 4.0, and 6.0 mL of  $\text{SiO}_2$  standard solution (see 42.2) to 50-mL volumetric flasks containing 30 to 35 mL of water and 1.5 to 1.6 mL of  $\text{HCl}$  (1 + 1); mix by swirling. Add 10 mL of ammonium molybdate solution from a pipet, gently swirling the solution. Dilute to volume and mix. Prepare a reference solution with the above reagents but without silica.

44.2 Two minutes after addition of the molybdate solution, measure the absorbance or percent transmittance relative to the reference solution at 400 nm in 1-cm cells.

44.3 *Standard Curve*—Plot the photometric readings of the standard solutions versus tenths of a milligram of  $\text{SiO}_2$ .

#### $\text{Al}_2\text{O}_3$ , $\text{CaO}$ , AND $\text{MgO}$ BY COMPLEXIOMETRIC TITRATION, AND $\text{BaO}$ , $\text{Na}_2\text{O}$ , AND $\text{K}_2\text{O}$ BY GRAVIMETRIC METHOD

##### 45. Reagents

45.1 *Ammonia (Buffer) Solution*—Dissolve 65 g of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) in 250 mL of water, add 570 mL of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), and dilute to 1 L. Store in a polyethylene bottle.

45.2 *Calcium Oxide Standard Solution* (1 mL = 1 mg  $\text{CaO}$ )—Dissolve 1.7848 g of primary standard reagent grade calcium carbonate ( $\text{CaCO}_3$ ), dried at 110°C, in 25 mL of water and 20 mL of  $\text{HCl}$  (1 + 1). Heat to a boil to remove  $\text{CO}_2$ , cool, and dilute to 1 L.



45.3 *EDTA Solution (Ethylenediaminetetraacetic Acid—Disodium Salt)* (for determination of CaO and MgO)—Dissolve 4 g of reagent in 1 L of water. Store in a polyethylene bottle. Standardize with the standard CaO and MgO solutions as follows:

45.3.1 *CaO*—Pipet 20 mL of CaO standard solution (1 mg/mL) to a 150-mL beaker, dilute to 50 to 60 mL, and proceed as described in 48.1; determination of CaO: mg CaO/mL EDTA = 20/titer.

45.3.2 *MgO*—Pipet 10 mL of MgO standard solution (1 mg/mL) to a 150-mL beaker, dilute to 50 to 60 mL, and proceed as described in 48.1; determination of MgO: mg MgO/mL EDTA = 10/titer.

45.3.3 One millilitre of EDTA solution will complex approximately 0.6 mg of CaO or 0.43 mg of MgO.

45.4 *Erichrome Black T (Indicator for Magnesium)*—A stable solution can be prepared by dissolving 0.1 g of indicator in 100 mL of triethanolamine. A dry mix likewise should be suitable (see Note 13).

45.5 *Hydroxylamine Hydrochloride (10 g/100 mL)*—Dissolve 10 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) in 100 mL of water.

45.6 *Hydroxy Naphthol Blue (Indicator for Calcium)*—This indicator can be purchased as a mix, or prepared by mixing 0.1 g with 100 g of NaCl (see Note 13).

45.7 *Magnesium Oxide, Standard Solution (1 mL = 1 mg MgO)*—Dissolve 0.6031 g of spectroscopically pure magnesium metal in 25 mL of HCl (1 + 4), and dilute to 1 L.

45.8 *Sodium Hydroxide Solution (20 g/100 mL)*—Dissolve 20 g of NaOH in 100 mL of water. Cool and store in a polyethylene bottle. The reagent should be as free of carbonate as practical.

45.9 *Triethanolamine Solution (30 %)*—Add water with stirring to 30 mL of triethanolamine ((HOCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N), diluting to 100 mL. Prepare fresh as needed.

NOTE 13—There are numerous indicators available and suitable for EDTA titrations, and their use is well documented in the literature. There is little advantage among them, and choice is generally one of preference. Perhaps the most general misuse of these indicators is the application of more indicator than necessary. The best guide is to use no more than a sufficient quantity to distinguish easily the color transition that takes place with the addition of about 3 to 4 drops of titrant.

## 46. Determination of BaO

### 46.1 Procedure:

46.1.1 Weigh 1.000 or 2.000 g of sample into a 75 or 100-mL platinum dish and proceed as described in 12.1.1. If a 1-g sample is used, only half the reagents specified are required; also, the use of H<sub>3</sub>BO<sub>3</sub> is not necessary. Heat the prepared solution, volume 100 to 125 mL in a 250-mL beaker, to boiling and add dropwise with stirring 10 mL of a 10 % solution of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) or 2 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1). Digest hot for 30 min, and cool to room temperature for 1 to 2 h. Filter through a 7-cm fine paper. Police the beaker with the aid of a bit of filter paper pulp and wash 6 to 8 times with cold water containing 2 to 3 drops of H<sub>2</sub>SO<sub>4</sub> per 100 mL. Discard the filtrate.

46.1.2 Transfer the precipitate to a tared crucible, carefully char the paper, and ignite at 800 to 900°C for 30 min. Cool and weigh as BaSO<sub>4</sub>.

46.1.3 *Calculation*—Calculate the percent of BaO as follows:

$$\text{BaO, \%} = \text{wt} \times 0.657 \times 100/\text{sample wt} \quad (19)$$

## 47. Preparation of Sample for Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O, and Determination of Al<sub>2</sub>O<sub>3</sub> by Complexometric Titration

47.1 *Procedure for Sample Preparation*— Prepare a 2.000-g sample as described in 12.1.1 (if Fe<sub>2</sub>O<sub>3</sub> is to be determined, see Note 14). To the dried residue after expulsion of HClO<sub>4</sub>, add 20 mL of hot water and 2 mL of HCl. Digest until salts have dissolved and transfer to a 200-mL volumetric flask. Cool and dilute to volume.

47.2 *Procedure for Determination of Al<sub>2</sub>O<sub>3</sub> by Complexometric Titration*—Transfer a 50-mL aliquot (equal to 0.5 g) to a 150- or 250-mL beaker and proceed as directed in Section 22.

## 48. Determination of CaO

48.1 *Procedure (Direct Titration)*—Transfer a 10-mL aliquot of the sample solution (equal to 0.1 g) to a 150-mL beaker, and dilute to approximately 75 mL. Place on a magnetic stirrer and stir at a moderate speed; a circle of filter paper placed under the beaker will aid in observing the end point (if barium is present in the sample, add 0.5 g of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>)). Add in sequence, 10 mL of 30 % triethanolamine, 1 mL of 10 % hydroxylamine hydrochloride, 4 mL of 20 % NaOH solution, and 0.1 to 0.2 g of hydroxy naphthol blue indicator mix. Titrate with EDTA until the solution is a pure blue color, free of reddish tint.

48.2 *Procedure (Back Titration)*—In the presence of much magnesium, a back titration will provide a sharper end point and better accuracy. Proceed as in 48.1, but add about 2 mL excess of EDTA after the end point is reached. Allow the solution to stir for several minutes; then titrate the excess of EDTA with the standard calcium solution until a reddish color appears. The true end point is not a complete change of blue to red but the first perceptible red color, indicating an excess of calcium ions.

### 48.3 Calculation:

48.3.1 *By Direct Titration*—Calculate the percent of CaO as follows:

$$\text{CaO, \%} = (\text{mL EDTA} \times \text{mg CaO})/\text{mL EDTA} \quad (20)$$

*Example*—If 16.5 mL of EDTA is added, then

$$16.5 \times 0.605 \text{ (1 mL EDTA} = 0.605 \text{ mg CaO)} = 9.98 \% \text{ CaO}$$

48.3.2 *By Back Titration*—Calculate the percent of CaO as follows:

$$\text{CaO, \%} = ((\text{mL EDTA} - \text{mL equiv Ca Std}) \times \text{mg CaO})/\text{mL EDTA}$$

*Example:*

17.9 mL EDTA (total added)

0.85 mL standard calcium solution (back titer)

1 mL calcium standard = 1.65 mL EDTA

equivalent of Ca standard = 0.85 × 1.65 = 1.40 mL EDTA

(17.9 – 1.40) × 0.605 = 9.98 % CaO

#### 49. Determination of MgO by Titration of CaO + MgO and Estimation of MgO by Difference

49.1 Transfer a 10-mL aliquot of the sample solution (equal to 0.1 g) to a 150-mL beaker and dilute to approximately 75 mL. Place on a magnetic stirrer and stir at a moderate speed (if barium is present, add 0.5 g of Na<sub>2</sub>SO<sub>4</sub>). Add in sequence 10 mL of 30 % triethanolamine, 1 mL of 10 % hydroxylamine hydrochloride, 4 mL of ammonium buffer, and 2 drops of erichrome black T indicator. Titrate with EDTA until the solution is a pure blue free of reddish tint.

49.2 *Calculation*—Calculate the percent of MgO as follows:

$$\text{MgO, \%} = \frac{\text{mL EDTA (CaO + MgO)} - \text{mL EDTA (CaO)}}{\times \text{mg MgO/mL EDTA}} \quad (21)$$

*Example:*

1 mL EDTA = 0.434 mg MgO

titer CaO = 16.5 mL EDTA

titer CaO+MgO = 20.3 mL

$(20.3 - 16.5) \times 0.434 = 1.6 \%$  MgO

#### 50. Determination of Na<sub>2</sub>O

50.1 Transfer a 5-mL aliquot (equal to 0.05 g) to a 50-mL platinum dish and determine Na<sub>2</sub>O as described in Section 32. If the expected percent of Na<sub>2</sub>O is less than 8 %, transfer a 10-mL aliquot (equal to 0.1 g) and proceed as described in Section 32.

#### 51. Determination of K<sub>2</sub>O

51.1 Transfer a 50-mL aliquot (equal to 0.5 g) to a 150-mL beaker, add 1.5 mL of HCl, and determine K<sub>2</sub>O as described in Section 33.

NOTE 14—There is also sufficient sample solution available to determine Fe<sub>2</sub>O<sub>3</sub> on a 0.5-g aliquot. However, this is not recommended unless the glass sample has been ground in an agate (or other nonferrous) mortar. If the sample is prepared free of iron contamination, a 0.5-g aliquot may be transferred to a 100-mL volumetric flask and Fe<sub>2</sub>O<sub>3</sub> determined by the 1,10-phenanthroline method (Section 19).

### BaO, Al<sub>2</sub>O<sub>3</sub>, CaO, AND MgO BY ATOMIC ABSORPTION; AND Na<sub>2</sub>O AND K<sub>2</sub>O BY FLAME EMISSION SPECTROSCOPY

#### 52. Instrumentation

52.1 *Atomic Absorption Spectrophotometers*—Commercially available instrumentation, utilizing the laminar flow burner principle, has reached a satisfactory degree of performance and quality. Most instruments can be operated in both an absorbance and emission mode. The more sophisticated instrumentation also provides background and curve correction and digital readout. Their most apparent weakness lies in imprecise gas flow regulation. Precision in readings and control of background can be improved by adding more precise controls to regulate pressure, flow and fuel/oxidant ratios. The capability to precisely repeat burner height adjustments is not always adequate on some instruments.

52.2 The following features are considered essential for glass analysis:

52.2.1 Operation in both the absorbance and emission modes.

52.2.2 Chart recorder.

52.2.3 Noise suppression.

52.2.4 Variable slit.

52.2.5 Monochromator, minimum dispersion of 33 Å/mm.

52.2.6 Analytical sensitivity to the potassium 766 nm emission line, less than 0.1 ppm K<sub>2</sub>O.

52.2.7 Capability to operate with both acetylene/air and acetylene/nitrous oxide fuel mixture.

52.3 In addition to the above, the following features are desirable:

52.3.1 A 0.5-m focal length monochromator.

52.3.2 Maximum dispersion of 15 Å/mm or better.

52.3.3 Signal averaging.

52.3.4 Curve and background correction.

52.3.5 Digital readout.

52.3.6 Wavelength scanning drive.

52.4 Presently available instrumentation, operated under optimum conditions, can be expected to give a precision of 0.5 to 1 %. Signal averaging circuitry is of great advantage in obtaining good precision. Accuracy is dependent not only on obtaining good precision but also in suppressing matrix effects. Buffering the solutions reduces matrix effects. However, it is advisable to test analyses with known standard reference materials or solutions of known composition similar to the samples under test. This will enable the analyst to determine if matrix effects are significant. Practically, the upper limit of oxide concentration in the sample for useful analysis is probably 10 to 20 %, depending on the established error of measurement and the usefulness of the result.

52.5 Manufacturers supply optimum instrumental operating conditions for specific elemental analysis. These include: fuel/oxidant mixtures; flame characteristics; burner adjustments; chemical interference and ionization suppressants; and optimal concentrations. These conditions should be followed closely. However, the operator should test his sample solutions for possible variation from these and determine his own best operational parameters. Published detection limits are usually beyond practical analytical capability. As a rule, analytical limits will be about ten times less sensitive than published detection limits.

#### 53. Reagents

53.1 *General Considerations:*

53.1.1 Stock solutions for standards are prepared from appropriate reagent quality materials as chlorides at a concentration of 1 mg/mL oxide (1000 ppm). They are preferably stored in polyethylene bottles, although slightly acidic solutions stored in borosilicate chemical glassware should be satisfactory. Appropriate dilutions are made as required for flame reference standards.

53.1.2 The amounts of HCl specified to dissolve the metal or carbonate used to prepare the standard solutions will normally provide a slight excess of acid. It is important that excess of HCl be controlled to not more than 1 mL, so that the subsequently prepared flame reference standards will contain, as practically as possible, 2 % HCl (20 mL/L). If insufficient acid is originally added, add not more than 0.5 mL at a time until solution is effected.

53.2 *Aluminum Oxide, Standard Solution (1 mL = 1 mg Al<sub>2</sub>O<sub>3</sub>)*—Dissolve 0.5293 g of spectroscopically pure aluminum metal in 12 mL of HCl (1 + 1) and dilute to 1 L. (If necessary, the addition of approximately 5 mg of mercuric chloride (HgCl<sub>2</sub>) will hasten the solution of aluminum metal.) 10 mL diluted to 1 L = 10 ppm Al<sub>2</sub>O<sub>3</sub>.

53.3 *Barium Oxide, Standard Solution (1 mL = 1 mg BaO)*—Dissolve 1.2871 g of spectroscopically pure barium carbonate (BaCO<sub>3</sub>), dried at 110°C, in 25 mL of water and 7 mL of HCl (1 + 4), heat to a boil to remove CO<sub>2</sub>, cool, and dilute to 1 L. 1 mL diluted to 1 L = 1 ppm BaO.

53.4 *Calcium Oxide, Standard Stock Solution (1 mL = 1 mg CaO)*—Dissolve 1.7848 g of primary standard reagent grade calcium carbonate (CaCO<sub>3</sub>), dried at 10°C, in 25 mL of water and 18 mL of HCl (1 + 4). Heat to a boil to remove CO<sub>2</sub>, cool, and dilute to 1 L.

53.5 *Calcium Oxide, Standard Solution (1 mL = 0.1 mg CaO = 100 ppm)*—Pipet 100 mL of the stock CaO solution into a 1-L volumetric flask and dilute to volume. 10 mL diluted to 1 L = 1 ppm CaO.

53.6 *Magnesium Oxide, Standard Stock Solution (1 mL = 1 mg MgO)*—Dissolve 0.6031 g of spectroscopically pure magnesium metal in 25 mL of HCl (1 + 4) and dilute to 1 L.

53.7 *Magnesium Oxide, Standard Solution (1 mL = 0.1 mg MgO = 100 ppm)*—Pipet 100 mL of the stock MgO solution into a 1-L volumetric flask and dilute to volume. 10 mL diluted to 1 L = 1 ppm MgO.

53.8 *Potassium Oxide, Standard Stock Solution (1 mL = 1 mg K<sub>2</sub>O)*—Dissolve 1.5829 g of potassium chloride (KCl), dried at 300°C, in 50 mL of water and 1 mL of HCl (1 + 1); dilute to 1 L.

53.9 *Potassium Oxide, Standard Solution (1 mL = 0.1 mg K<sub>2</sub>O = 100 ppm)*—Pipet 100 mL of the stock K<sub>2</sub>O solution into a 1-L volumetric flask and dilute to volume. Two millilitres diluted to one litre = 0.2 ppm K<sub>2</sub>O.

53.10 *Sodium Oxide, Standard Stock Solution (1 mL = 1 mg Na<sub>2</sub>O)*—Dissolve 1.7101 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), dried at 300°C, in 25 mL of water and 15 mL of HCl (1 + 4); heat to boiling to remove CO<sub>2</sub>, cool, and dilute to 1 L.

53.11 *Sodium Oxide, Standard Solution (1 mL = 0.05 mg Na<sub>2</sub>O = 50 ppm)*—Pipet 50 mL of the stock Na<sub>2</sub>O solution into a 1-L volumetric flask and dilute to volume. Twenty millilitres diluted to one litre = 1 ppm Na<sub>2</sub>O; 1.0 mL = 0.05 ppm Na<sub>2</sub>O.

## 54. Flame Buffer Solutions

54.1 *Atomic Absorption (AA) Buffer Solution (5 g of La<sub>2</sub>O<sub>3</sub>, 20 mL of HCl, and 10 g of KCl per L)*—This solution should be prepared in large quantities. It is used to dissolve and dilute samples prepared for the atomic absorption determination of BaO, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO. For preparation of 10 L: Weigh 108.5 g of lanthanum chloride (LaCl<sub>3</sub>·6H<sub>2</sub>O) (Note 17) and 100 g of potassium chloride (KCl) and transfer to a 1-L volumetric flask (preferably calibrated to deliver). Add about 500 mL of water and dissolve the salts. Add 200 mL of HCl, cool if necessary, and dilute to volume, or to the “to deliver” mark. Drain into a container that will hold 10 L (preferably of polyethylene). With the same flask, add 9 L more of water. Thoroughly mix the solution. The container should be fitted

with a siphon or spigot for dispensing the solution. When not in use, it must be sealed tightly to avoid evaporation loss.

NOTE 15—**Caution:** Lanthanum chloride reagent, even of the best purity, usually contains traces of calcium and lesser amounts of aluminum and magnesium as impurities. For this reason, it is advisable to prepare sufficient quantities of solutions from the same lot to accommodate a large number of determinations. It is also important to weigh the reagent and dispense solutions accurately so that standards and samples contain equal added concentrations of impurities which can be considered as background. Since a bracketing technique is used in comparing standards and sample, error is canceled. However, if the buffer solution used to prepare samples, and the lanthanum solution used to prepare the standards contribute different amounts of calcium, aluminum, or magnesium to the solutions prepared from them, the respective backgrounds will differ, and results can be in error. New lots of LaCl<sub>3</sub> should be checked for purity and, if necessary, new standards and buffer solutions prepared from the same lot.

54.2 *Lanthanum Chloride Solution for AA Standards (100 g La<sub>2</sub>O<sub>3</sub>/L)*—This solution is used for the preparation of atomic absorption reference standards. For preparation of 2 L, weigh 434.0 g of LaCl<sub>3</sub>·6H<sub>2</sub>O and transfer to a 2-L volumetric flask. Dissolve in about 1 L of water, add 2 mL of HCl, and dilute to volume. Fifty millilitres diluted to one litre = 5 g La<sub>2</sub>O<sub>3</sub>/L.

54.3 *Potassium Chloride Solution for AA Standards (200 g/L)*—Prepare 2 L. Weigh 400 g of KCl and transfer to a 2-L volumetric flask. Dissolve in water and dilute to volume. Fifty millilitres diluted to one litre = 10 g KCl/L.

54.4 *Potassium Buffer Sodium Chloride Solution*—This solution is used for the flame emission determination of K<sub>2</sub>O. Dissolve 189 g of NaCl in water and dilute to volume in a 1-L volumetric flask. Ten millilitres diluted to one litre equals a concentration of approximately 1000 ppm Na<sub>2</sub>O.

54.5 *Sodium Buffer Potassium Chloride Solution (159 g/L)*—This solution is used for the flame emission determination of Na<sub>2</sub>O. Dissolve 159 g of KCl in water and dilute to volume in a 1-L volumetric flask. Ten millilitres diluted to one litre equals a concentration of approximately 1000 ppm K<sub>2</sub>O.

NOTE 16—**Caution:** In keeping with the importance of obtaining samples and standards containing identical concentrations of lanthanum, accurate dilution of the buffer solution is necessary. Use of a flask calibrated “to deliver” is the most simple and best way to accomplish this. Error is about 0.5 mL/L. Conversely, the error for dispensing from a 2000-mL graduated cylinder may be 10 mL. For 10 L, this is 5 mL versus 50 mL, which is significant.

## 55. Flame Spectrophotometry (Atomic Absorption and Emission)

### 55.1 General Considerations:

55.1.1 **Table 1** outlines instrument and sample parameters to be used for analysis. Optimum oxidant and fuel ratios and burner height should be determined by consulting the manufacturer’s instructions. These two parameters can be expected to differ between instruments because of atomizer and burner configuration.

55.1.2 **Table 2** outlines the equivalent concentration of the sample solution for each oxide; the normal range of each oxide as ppm in the sample solution and as weight percent in the sample itself; and finally, the concentrations of reference standards to cover the normal range in steps for bracketing. The table is designed to cover most of the soda-lime glasses



**TABLE 1 Parameters for Flame Spectrophotometry**

Mode	Element	Oxidant/ Fuel	Full Scale		Base Solution		Analytical Line, nm
AA <sup>A</sup>	BaO	N <sub>2</sub> O/A	1 to 50	0.5 % La	2 % HCl	1 % KCl	554
AA	Al <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O/A	5 to 50	0.5 % La	2 % HCl	1 % KCl	309
AA	CaO	N <sub>2</sub> O/A	0.5 to 5	0.5 % La	2 % HCl	1 % KCl	422
AA	MgO	N <sub>2</sub> O/A	0.1 to 2	0.5 % La	2 % HCl	1 % KCl	285
FE <sup>B</sup>	K <sub>2</sub> O	Air/A	0.1 to 2.0	0.5 % La	2 % HCl	1000 ppm Na <sub>2</sub> O	766 to 769
FE	Na <sub>2</sub> O	Air/A	0.1 to 2.0	0.5 % La	2 % HCl	1000 ppm K <sub>2</sub> O	589.2

<sup>A</sup> Atomic absorption.

<sup>B</sup> Flame emission.

**TABLE 2 Concentrations of Sample and Reference Standards for Flame Spectrophotometry**

	Sample Concentration Equivalent, g/L	Normal Range Oxide, Sample Solution, ppm	Normal Range Oxide in Sample, weight%	Concentration of Reference Standards, ppm	Concentration Equivalent, Oxide in Each Bracket, %
BaO	2	2 to 15	0.1 to 0.75	2, 5, 10, 15	0.25
Al <sub>2</sub> O <sub>3</sub>	1	10 to 30	1 to 3	10, 15, 20, 25, 30	0.5
CaO	0.02	1 to 3	5 to 15	1, 2, 3	5
MgO (less than 1 %)	0.1	0.1 to 1	0.1 to 1	0.1, 0.5, 1.0	0.5
MgO (greater than 1 %)	0.02	0.2 to 1.2	1 to 6	0.2, 0.5, 1.0, 1.2	2.5
K <sub>2</sub> O	0.1	0.2 to 2	0.2 to 2	0.2 to 2 in steps of 0.2	0.2
Na <sub>2</sub> O	0.01	1.2 to 1.6	12 to 16	1.2 to 1.6 in steps of 0.05	0.5

commonly found in commerce. It can be used as a guide for glasses whose composition may be outside the ranges noted; adjustment of sample size and dilution, and choice of reference standard concentration within instrument capability should enable a somewhat broader range of compositions to be determined.

55.2 Bracketing refers to the common practice of comparing the sample to two reference standards, one of which is of a concentration slightly greater and one slightly less than the sample. It is assumed that instrument response is, for practical purposes, linear between the two reference standards. The bracketing steps given in **Table 2** should provide practical linear response. In the atomic absorption mode, response can be expected to be linear over the entire range of concentrations. In the emission mode, response over the entire range may be slightly curved, but not sufficiently so to require correction between brackets.

## 56. Flame Reference Standards

56.1 *General Considerations*—Reference standards are prepared by adding the appropriate buffer solutions, acid, and standards to provide the concentration ranges as outlined in **Table 2**. In practice, it is necessary to prepare only those known to be needed. However, it is essential to have sufficient reference standards to bracket samples and establish the performance characteristics of the instrument.

56.2 *Reference Standard Solutions for the Determination of BaO, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO by Atomic Absorption*—Pipet into 1-L volumetric flasks 50 mL of LaCl<sub>3</sub> solution (100 g/L), 50 mL of KCl solution (200 g/L), 20 mL of HCl (added from a pipet or buret), and then the appropriate volumes of the oxide standard solutions to provide the required concentrations. Dilute to volume and mix. Reference standards for BaO and Al<sub>2</sub>O<sub>3</sub> are prepared from the 1000-ppm standard solutions; reference standards for CaO and MgO from the 100-ppm standard solutions.

56.3 *Reference Standard Solution for K<sub>2</sub>O*—Pipet, or add by a buret, into a 1-L volumetric flask containing about 200 mL of water, 10 mL of the potassium buffer NaCl solution (189 g/L), 20 mL of HCl, and then the appropriate volumes of the 100-ppm K<sub>2</sub>O standard solution. Dilute to volume and mix.

56.4 *Reference Standard Solution for Na<sub>2</sub>O*—Pipet, or add by a buret, into a 1-L volumetric flask containing about 200 mL of water, 10 mL of the sodium buffer KCl solution (159 g/L), 20 mL of HCl, and then the appropriate volumes of the 50-ppm Na<sub>2</sub>O standard solution. Dilute to volume and mix.

NOTE 17—It is convenient to designate the reference samples in equivalent percent oxide as well as concentration in parts per million. If the instrument is equipped with digital readout, absorbance or emission usually can be adjusted to read directly in percent.

## 57. Preparation of Sample Solutions for the Determination of BaO, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO

### 57.1 Procedure:

57.1.1 Weigh 0.2000 g of sample into a 50 or 75-mL platinum dish, moisten with 2 mL of water, and add 3 mL of HF and 5 mL of HClO<sub>4</sub> while stirring with a platinum or plastic rod. Evaporate uncovered until fluorides begin to react, then cover with a platinum lid, allowing just sufficient space for HF to escape. When all reaction has subsided, cool, rinse off the lid and sides of the dish, stir, and evaporate to dryness. Cool slightly, rinse the sides of the dish with a minimum of water, add 3 to 4 mL of HClO<sub>4</sub>, and again evaporate to dryness. It is essential to eliminate all traces of fluoride to avoid subsequent flame interference. Cool, dissolve the residue in about 20 mL of the atomic absorption (AA) buffer solution (54.1) and transfer to a 100-mL volumetric flask using buffer solution to rinse the platinum dish. Dilute to volume with the AA buffer solution.

57.1.2 *For Determination of BaO*—The sample solution is of suitable concentration for the determination of BaO. Sample

concentration is equivalent to 2 g/L. Appropriate dilutions are made for the determination of the other oxides.

57.1.3 *For Determination of Al<sub>2</sub>O<sub>3</sub>*—Transfer 25 mL of the sample solution to a 50-mL volumetric flask and dilute to volume with the AA buffer solution. This sample solution is suitable for the determination of Al<sub>2</sub>O<sub>3</sub>. Sample concentration = 1 g/L.

57.1.4 *For Determination of CaO*—Transfer 5 mL of the sample solution to a 500-mL volumetric flask and dilute to volume with AA buffer solution. Sample concentration = 0.02 g/L.

57.1.5 *For Determination of MgO that is less than 1.0 %*—Transfer 5 mL of the sample solution to a 100-mL volumetric flask and dilute to volume with AA buffer solution. Sample concentration = 0.1 g/L.

57.1.6 *For Determination of MgO that is more than 1.0 %*—Use the sample solution prepared for the determination of CaO (57.1.4).

## 58. Preparation of Sample Solutions for the Determination of Na<sub>2</sub>O and K<sub>2</sub>O

### 58.1 Procedure:

58.1.1 Weigh 0.1000 g of sample into a 50 or 75-mL platinum dish, moisten with 1 mL of water, and add 2 to 3 mL of HF and 5 mL of HClO<sub>4</sub> while stirring with a platinum or plastic rod. Evaporate as described in 56.1; however, repeating the evaporation with additional HClO<sub>4</sub> is not necessary. Dissolve the dry residue in 10 to 15 mL of water and 2 mL of HCl. Transfer to a 100-mL volumetric flask. This solution is further diluted for the determination of Na<sub>2</sub>O and K<sub>2</sub>O.

58.1.2 *For Determination of Na<sub>2</sub>O*—Transfer 10 mL of the sample solution to a 1-L volumetric flask containing about 200 mL of water, add 10 mL of the sodium buffer KCl solution (159 g/L), and 19.8 mL of HCl from a buret. Dilute to volume and mix. Sample concentration = 0.01 g/L.

58.1.3 *For Determination of K<sub>2</sub>O*—Transfer 10 mL of the sample solution to a 100-mL volumetric flask, add 1 mL of the potassium buffer NaCl solution (189 g/L), and 1.8 mL of HCl from a buret. Dilute to volume and mix. Sample concentration = 0.1 g/L.

## 59. Comparison of Samples to Reference Standards

59.1 Adjust the instrument to the proper operating parameters for the element oxide to be determined as recommended in the manufacturer's instructions. The instrument is operated in the absorption mode for the determination of BaO, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO, and in the emission mode for Na<sub>2</sub>O and K<sub>2</sub>O. When stability of response has been achieved, obtain at least three separate readings of the sample and of two reference standards that "bracket" the sample reading. Average the sample and standards readings and estimate the sample concentration by interpolation. The "bracketing" comparison technique should be observed regardless of how data are recorded: meter reading, chart recorder, or digital readout. The manufacturer's instructions on handling data, background, and curve correction, if any, should be observed.

## SO<sub>3</sub> (TOTAL SULFUR)

### 60. Procedure

60.1 Prepare a 2 or 3-g sample as described in Section 34 and dilute to 200 mL in a 400-mL beaker. Heat to boiling and add slowly 10 mL of 10 % BaCl<sub>2</sub> solution while stirring the solution. Digest covered for 30 min, and cool for 1 to 2 h. Filter the precipitate on a 7 or 9-cm fine filter paper. Carefully transfer all the precipitate to the filter with the aid of a bit of paper pulp. Wash 6 to 8 times with cold water.

60.2 Transfer the precipitate to a tared crucible; char and ignite at 700 to 800°C for 30 min. Cool in a desiccator and weigh as BaSO<sub>4</sub>.

60.3 *Calculation*—Calculate the percent of SO<sub>3</sub> as follows:

$$\text{SO}_3, \% = \text{wt} \times 0.343 \times 100/\text{wt of sample} \quad (22)$$

## DETERMINATION OF B<sub>2</sub>O<sub>3</sub>

### 61. Reagents

61.1 *Hydrochloric Acid* (approximately 0.1 N)—Dilute 8.5 mL of HCl to 1 L with CO<sub>2</sub>-free water.

61.2 *Mannitol*, reagent grade.

61.3 *Sodium Hydroxide* (approximately 6 N)—Prepare an approximate 6 N NaOH solution, 240 g/L, free of CO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. This solution should be prepared and stored in plastic containers because NaOH solutions attack borosilicate glassware.

61.4 *Sodium Hydroxide Solution* (approximately 1 N)—Dilute 1 part of the 6 N NaOH solution with 5 parts of CO<sub>2</sub>-free water and store in a plastic container.

61.5 *Sodium Hydroxide, Standard Solution (0.05 N)*—Prepare an approximate 0.05 N NaOH solution, 2 g/L, free of CO<sub>2</sub>, and store in a plastic container. Standardize against NIST SRM No. 84h acid potassium phthalate using phenolphthalein indicator.

61.6 *Sodium Hydroxide, Standard Solution (0.1 N)*—Prepare and standardize an approximate 0.1 N NaOH solution, 4 g/L, as for the 0.05 N NaOH standard solution.

### 62. Procedure

62.1 Weigh 1.000 g of sample and 3 g of Na<sub>2</sub>CO<sub>3</sub>, and transfer to a suitable platinum dish or crucible. Mix well, cover, and heat gradually over a burner until a clear melt is obtained. Rotate the dish or crucible so that the melt solidifies in a thin layer. Cover and cool. Place the crucible, if used, in a 250-mL beaker. Add 15 mL of HCl (1 + 1) to the cold melt, cover, and digest at room temperature until the melt has disintegrated. Transfer the solution to a 250-mL beaker. Rinse the dish and cover with cold water. If particles of fusion mass adhere to the cover, which is used during fusion, remove these with the aid of a policeman. Dilute to about 80 mL.

62.2 Adjust to a pH between 5.0 and 5.5 with 6 N and 1 N NaOH solution and 0.1 N HCl, using a pH meter or a suitable indicator (bromocresol purple is excellent, as the color is greenish in the desired pH range). Digest on a hot plate or steam bath at a temperature of 65 to 95°C for 20 to 30 min, making sure that the pH remains in the 5.0 to 5.5 range throughout the digestion by further additions of 0.1 N HCl if necessary. Bubble a stream of CO<sub>2</sub>-free air through the solution

during the digestion period to eliminate CO<sub>2</sub> and prevent bumping. Filter through an 11-cm coarse paper, using a platinum cone and suction if desired, and collect the filtrate in a 400-mL beaker. Transfer the gel to the paper and wash 8 to 10 times with hot water. Final volume of the filtrate should be 200 to 225 mL.

62.3 Cool the solution to room temperature. Adjust the pH with a pH meter with 0.1 N HCl and 0.05 N NaOH solution added from a buret. When a stable pH of 5.4 is obtained, record the buret reading. Add 40 g of mannitol to the solution and titrate with the 0.05 N NaOH solution until a pH of 6.8 is reached. The volume of NaOH solution required between pH 5.4 and pH 6.8 provides the measure of B<sub>2</sub>O<sub>3</sub> contained in the sample.

62.4 *Calculation*—Calculate the percent of B<sub>2</sub>O<sub>3</sub> as follows:

$$B_2O_3, \% = [(0.03482 \times V \times N)/W] \times 100 \quad (23)$$

where:

V = standard NaOH solution required for titration between pH 5.4 and 6.8 mg,

N = normality of the NaOH solution, and

W = sample, g.

62.5 *Blank Titration*—The titer of the sample shall be corrected by a blank titer determined on a sample of glass known to contain no B<sub>2</sub>O<sub>3</sub> by following the above procedure.

NOTE 18—The above procedure is satisfactory for the analysis of glasses containing not more than 5 % B<sub>2</sub>O<sub>3</sub>. In the analysis of glasses higher in B<sub>2</sub>O<sub>3</sub>, weigh a 0.5-g sample and titrate with 0.1 N NaOH solution. It is also necessary to apply a correction factor to the calculation when glasses high in B<sub>2</sub>O<sub>3</sub> are analyzed. This correction factor should be determined by each analyst himself, based on his analysis of NIST SRM No. 93 or 93a (corrected for ignition loss at 800°C).

NOTE 19—If the glass contains fluorine, or other anions or anionic complexes that may consume alkali when titrated between pH 5.4 and 6.8, the titration can be made by adjusting the pH to 6.3, then adding mannitol and titrating back to pH 6.3. Since not all the boric acid is titrated, a volumetric correction is added to the titer based on the millilitres of titrant used as follows:

Titrant Used, mL	Correction, mL	Titrant Used, mL	Correction, mL
1	0.05	14	0.26
2	0.08	16	0.29
4	0.13	18	0.31
6	0.16	20	0.33
8	0.19	24	0.36
10	0.22	28	0.40
12	0.24		

The correction required in Note 18 is also made, if necessary.

## FLUORINE BY PYROHYDROLYSIS SEPARATION AND SPECIFIC ION ELECTRODE MEASUREMENT

### 63. Reagents

63.1 *Fluoride Standard Solution A* (1 mL = 1 mg F = 1000 ppm)— Heat about 5.0 g of sodium fluoride (NaF) in a platinum crucible at 450 to 500°C for 15 min. Cover, and cool in a desiccator. Weigh 2.2152 g of NaF, transfer to a 1000-mL volumetric flask, dissolve, and dilute to volume. Transfer and store in a polyethylene bottle.

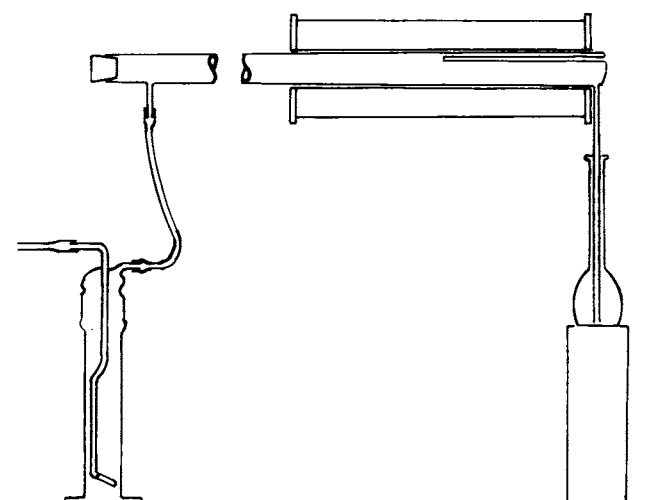


FIG. 1 Apparatus for Pyrohydrolysis of Fluorine

63.2 *Fluoride Standard Solution B* (1 mL = 0.01 mg F = 10 ppm)— Pipet 10 mL of standard fluoride solution A to a 1000-mL volumetric flask. Dilute to volume, mix, and store in a polyethylene bottle.

63.3 *Sodium Chloride-Sodium Acetate Buffer Solution* (pH 5.5)—Weigh 60 g of sodium chloride (NaCl) and 70 g of sodium acetate (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) and dissolve in about 900 mL of water. Adjust to a pH of 5.5 by the addition of acetic acid using a pH meter. Dilute to 1000 mL. Prepare 2 to 3 L of this solution and store in a polyethylene bottle.

63.4 *Sodium Hydroxide Solution* (0.1 N)—Dissolve 4.0 g of sodium hydroxide (NaOH) in 1 L of water and store in a polyethylene bottle.

63.5 *Uranium Oxide*—Prepare uranium oxide (U<sub>3</sub>O<sub>8</sub>) by heating uranyl acetate (UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O) in a platinum dish at 300°C for 1 h and then at 700°C for 3 h; 150 g of uranyl acetate will yield 100 g of U<sub>3</sub>O<sub>8</sub>.

### 64. Apparatus (see Fig. 1)

64.1 *Tube Furnace*—A split tube furnace with a heating chamber 1½ in. (38 mm) in diameter by 12 in. (305 mm) long, operable at 1000°C or preferably 1150°C, and provided with suitable temperature control.

64.2 *Combustion Tube*—Fused high-silica glass, 30 mm in outside diameter by 22 in. (560 mm) long, sealed at one end. A 10-in. (254-mm) length of 10-mm outside diameter tubing (exit) is sealed at right angles at the closed end of the tube. A 2-in. (50-mm) length of 7-mm outside diameter tubing (inlet) is sealed 2 in. from the open end of the tube. When assembled, the sealed (exit) end is kept tight against one end of the furnace, maintaining it hot enough to avoid condensation of fluoride. The open end of the tube is closed with a rubber stopper. It also is convenient to seal a thermocouple well of 7-mm outside diameter tubing, 7 in. (178 mm) long into the closed end of the tube.

64.3 *Gas Scrubbing Bottle*,<sup>7</sup> with 125-mL cap with a coarse fritted disk. The bottle is maintained about ¾ filled with water.

<sup>7</sup> A bottle similar to Corning No. 31760 or Kimble No. 28215 has been found satisfactory.



64.4 *Oxygen Cylinder Gas*—The cylinder should be provided with a two-stage reducing valve and a gas-flow regulator for a flow rate of 1 to 10 ft<sup>3</sup>/h.

64.5 *Fluoride Specific Ion Electrode and Reference Electrode*—Several are available commercially. Both the specific ion and reference electrode should be of the same manufacture and the manufacturer's operating instructions should be followed in their use.

64.6 *Electrometer*—There are numerous commercially available pH meters and electrometers designed to make specific ion measurements. The manufacturer's operating instructions should be followed.

64.7 *Combustion Boat*—A 3½-in. (89-mm) long by ½-in. (12.7-mm) wide combustion boat of platinum or heavy-duty nickel is satisfactory.

## 65. Procedure for Pyrohydrolysis

65.1 Weigh 1.000 g of glass powder (through 200 mesh) and transfer to an agate mortar. Weigh 3 g of U<sub>3</sub>O<sub>8</sub>, transfer about 1 g to the mortar, and intimately mix by grinding. Transfer to a piece of glazed paper; rinse the mortar by two successive additions of the remaining U<sub>3</sub>O<sub>8</sub>, and transfer each addition to the paper. Finally, mix well on the paper and transfer evenly over the bottom of the combustion boat. Carefully brush all sample material from the mortar and paper to avoid loss.

65.2 Bring the furnace to a temperature of 1000°C, or preferably 1150°C. Pipet 10 mL of 0.1 N NaOH solution into a 100-mL plastic volumetric flask and add 50 mL of water (Note 19). Regulate the oxygen flow to 3 to 4 ft<sup>3</sup>/h. Place the flask under the exit tube so that it extends to the bottom of the flask. The exit tube should also be touching the end of the furnace. Insert the sample into the center of the hot zone and close the open end of the tube with a rubber stopper. Pyrohydrolyze for 45 min.

65.3 When pyrohydrolysis is complete, remove the absorbing solution from under the exit tube and rinse off the outside of the tube. Carefully neutralize the solution with 0.1 N HCl to the phenolphthalein end point; add 10 mL of the pH 5.5 buffer and dilute to volume.

NOTE 20—Ten millilitres of 0.1 N NaOH solution is satisfactory to absorb up to 1.5 % fluorine (15 mg) in a 1-g sample and still provide a slight excess. If more fluorine is expected, use 20 mL of NaOH solution for up to 3.5 % fluorine. For higher amounts, weigh a 0.5-g sample and use 20 mL of NaOH solution. This will be satisfactory for fluorine opal glasses which usually contain 5 to 6 % fluorine. Add 40 mL of water to 20 mL of NaOH solution to maintain a 60-mL volume during pyrohydrolysis.

## 66. Procedure for Specific Ion Measurement

### 66.1 Calibration Solutions:

66.1.1 *Calibration Solution (1 mL = 1 mg F = 1000 ppm)*—Weigh 2.2152 g of dried NaF (see 63.1); transfer to a 1000-mL volumetric flask, dissolve and dilute to about 800 mL. Add 100 mL of sodium chloride-sodium acetate buffer, pH 5.5; dilute to volume and mix. Immediately transfer and store in a polyethylene bottle.

66.1.2 *Calibration Solution (1 mL = 0.1 mg F = 100 ppm)*—Pipet 100 mL of standard fluoride solution A to a 1000-mL volumetric flask. Add 100 mL of pH 5.5 buffer, dilute to volume, and mix. Store in a polyethylene bottle.

66.1.3 *Calibration Solution (1 mL = 0.01 mg F = 10 ppm)*—Pipet 10 mL of standard fluoride solution A into a 1000-mL volumetric flask. Add 100 mL of pH 5.5 buffer, dilute to volume, and mix. Store in a polyethylene bottle.

66.1.4 *Calibration Solution (1 mL = 0.001 mg F = 1 ppm)*—Pipet 100 mL of standard fluoride solution B into a 1000-mL volumetric flask. Add 100 mL of pH 5.5 buffer, dilute to volume, and mix. Store in a polyethylene bottle.

66.1.5 *Calibration Solution (1 mL = 0.0001 mg F = 0.1 ppm)*—Pipet 10 mL of standard fluoride solution B into a 1000-mL volumetric flask. Add 100 mL of pH 5.5 buffer, dilute to volume, and mix. Store in a polyethylene bottle.

66.1.6 *Calibration Solution (1 mL = 0.00007 mg F = 0.07 ppm)*—Pipet 7 mL of standard fluoride solution B into a 1000-mL volumetric flask. Add 100 mL of pH 5.5 buffer, dilute to volume, and mix. Store in a polyethylene bottle.

66.1.7 *Calibration Solution (1 mL = 0.00004 mg F = 0.04 ppm)*—Pipet 4 mL of standard fluoride solution B into a 1000-mL volumetric flask. Add 100 mL of pH 5.5 buffer, dilute to volume, and mix. Store in a polyethylene bottle.

### 66.2 Measurement:

66.2.1 Set up the electrodes and meter as described in the manufacturer's instructions. Transfer 20 to 25 mL of the calibrating solution to a 50 or 100-mL polyethylene beaker. Add a small magnetic stir bar, place the beaker on a magnetic stirrer, and stir at a slow to moderate speed. Insert the electrodes and measure the millivolt response when equilibrium is reached (usually within 1 min).

66.2.2 Plot response of the calibrating solutions on semi-log paper, millivolts on the linear scale, and concentrations of ppm fluorine on the logarithmic scale. Response of the electrode is negative to increasing concentration of fluoride. A proper responsive electrode should give a difference of about 59 mV per ten-fold increase or decrease in concentration over the range from 0.1 ppm F to 1000 ppm F. Below a concentration of 0.1 ppm, F response is usually nonlinear. A concentration of 0.04 ppm F is generally the lowest limit of practical measurement.

66.2.3 Samples are measured identically to the calibrating solutions. In practice, it is only necessary to bracket the sample readings with the necessary number of calibration solutions. Calibration should be made each time samples are analyzed to correct for possible drift of electrode response. Read concentration of sample solutions from the calibration graph—millivolts vs. concentration.

66.3 *Calculation*—Calculate the percent of fluorine as follows:

$$\text{Fluorine, \%} = \text{ppm sample} / (100 \times \text{sample wt}) \quad (24)$$

### Example:

95 ppm found in sample  
1 g sample taken  
 $95 / (100 \times 1) = 0.95 \%$

NOTE 21—Care of the fluoride electrode: If the electrode appears sluggish, it may be cleaned by gently polishing the crystal surface with a water paste of cerium oxide. An electrode that has not been used for some time may be soaked a few hours in a solution of about 2 ppm fluoride. If used frequently, it may be kept in such a solution. Response is particularly improved for low concentrations by this pretreatment.

**P<sub>2</sub>O<sub>5</sub> BY THE MOLYBDO-VANADATE METHOD**

**67. General Considerations**

67.1 Commercial soda-lime glasses contain only traces of phosphate (P<sub>2</sub>O<sub>5</sub>). P<sub>2</sub>O<sub>5</sub> is determined without prior separations. The interference of arsenic is negligible; approximately 0.6 % As<sub>2</sub>O<sub>3</sub> as arsenate can be tolerated in a 1-g sample. The range from 0.00 to 0.04 % P<sub>2</sub>O<sub>5</sub> is determined by using absorbance cells of 5-cm light path; and up to 0.20 % P<sub>2</sub>O<sub>5</sub> with the use of 1-cm cells.

**68. Reagents**

68.1 *Molybdate Reagent Solution*—Dissolve 50 g of ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O), or 65 g of sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) in 500 mL of water (warm if necessary). Dilute to 1 L and store in a polyethylene bottle.

68.2 *Phosphate Standard Solution (1 mL = 1 mg P<sub>2</sub>O<sub>5</sub>)*—Dissolve 1.9173 g of potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), dried at 110°C, in water and dilute to 1 L. Store in a polyethylene bottle.

68.3 *Phosphate Standard Solution (1 mL = 0.1 mg P<sub>2</sub>O<sub>5</sub>)*—Dilute 100 mL of standard phosphate solution (1 mL = 1 mg P<sub>2</sub>O<sub>5</sub>) to 1 L. Store in a polyethylene bottle.

68.4 *Vanadate Reagent Solution*—Dissolve 2.5 g of ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>) in 50 mL of water (warm if necessary). Cool, add 20 mL of HNO<sub>3</sub>, and dilute to 1 L. Store in a polyethylene bottle.

**69. Procedure**

69.1 Weigh 1 g of sample into a 50 to 75-mL platinum dish; add 2 mL of water, 5 to 6 mL of HF, 5 to 6 mL of HClO<sub>4</sub>, and 2 to 3 mL of HNO<sub>3</sub>, and proceed as described in 11.1.1. Evaporate just to dryness. To the dry residual add 5 mL of HNO<sub>3</sub> (1 + 2) and 5 mL of water. Warm until the salts have dissolved. Transfer the solution to a 50-mL volumetric flask. If the solution is cloudy, add a bit of paper pulp and filter through a 5.5-cm fine filter paper into the flask and wash 3 to 4 times with cold water.

69.2 Cool, add by pipet 5 mL of vanadate solution, and mix; add 5 mL of molybdate solution and mix. Dilute to volume, mix, and after 5 min, measure absorbance or percent transmittance at 460 nm. Use 10 or 50-mm absorption cells as appropriate. Prepare a reagent blank as the photometric reference. Compare to the standard curve.

69.3 *Calculation*—Calculate the percent of P<sub>2</sub>O<sub>5</sub> as follows:

$$P_2O_5, \% = (\text{mg } P_2O_5/\text{wt of sample}) \times 0.1 \quad (25)$$

**70. Preparation of Standard Curve**

70.1 *For the Range from 0.00 to 0.04 % P<sub>2</sub>O<sub>5</sub>*—Prepare a series of 50-mL volumetric flasks containing 0.0, 0.1, 0.2, 0.3, and 0.4 mg of P<sub>2</sub>O<sub>5</sub> and 5 mL of HNO<sub>3</sub> (1 + 2). Dilute to about 30 mL and proceed as in 69.2. Measure absorbance or percent transmittance in absorption cells of 5-cm light path. (The expected absorbance for 0.4 mg of P<sub>2</sub>O<sub>5</sub> is approximately 0.400.) The 0.00 P<sub>2</sub>O<sub>5</sub> solution is the photometric reference. Plot absorbance vs P<sub>2</sub>O<sub>5</sub> in 0.1-mg units on linear graph paper, or percent transmittance on semi-log graph paper.

70.2 *For 0.0 to 0.2 % P<sub>2</sub>O<sub>5</sub>*—Prepare a series of 50-mL volumetric flasks containing 0.0, 0.5, 1.0, 1.5, and 2.0 mg of

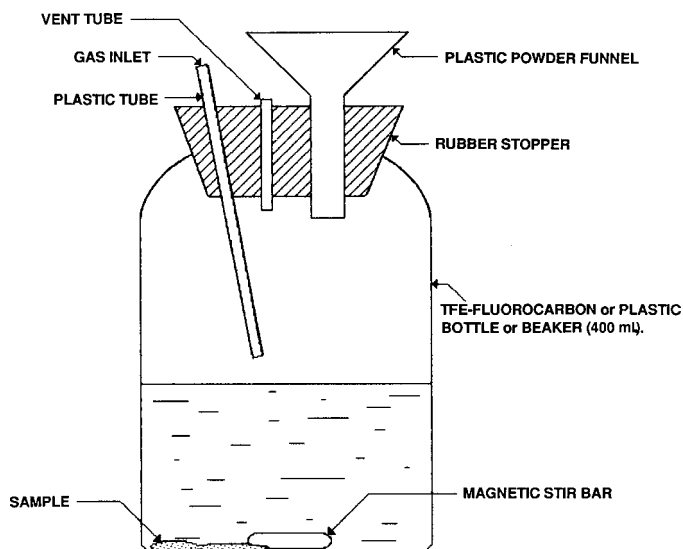


FIG. 2 Ferrous Iron Reaction Vessel

P<sub>2</sub>O<sub>5</sub> and proceed as described in 69.1, except use absorption cells of 1-cm light path.

**COLORIMETRIC DETERMINATION OF FERROUS IRON USING 1,10 PHENANTHROLINE**

**71. General Considerations**

71.1 Equilibrium conditions in soda-lime flint glass are such that the majority of the total iron is present as the oxidized species ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) with a small fraction in the reduced ferrous oxide (FeO) state. With this procedure, it is possible to determine the reduced iron by the spectrophotometric measurement of the 1,10 Phenanthroline iron complex.

71.2 To avoid contamination with iron, the sample should be ground in an agate container to pass a No. 200 sieve. Consideration should be given to grinding the material in some media, for example, carbon tetrachloride, to decrease the possibility of localized heating of the glass particles which may oxidize portions of the ferrous iron.

71.3 Time is critical in this procedure from the initial purging through the addition of the 1,10 phenanthroline. The time listed in 74.1 should be strictly adhered to.

**72. Apparatus (see Fig. 2)**

72.1 *Reaction Vessel*—Plastic or TFE-fluorocarbon bottle or beaker of 400-mL capacity. The vessel will be used to exclude air (oxygen) when reacting the sample with the reagents. The vessel can be fitted with a rubber stopper as shown in Fig. 2 or the vessel can be a beaker with the lip removed and the bottom of another container placed on top with the appropriate openings for introduction of purge gas, reagents, and vent tubing.

72.2 *Plastic Tube*—The plastic tube is used to introduce the purge gas into the vessel. It is advisable to use a connection between the plastic tubing and the gas cylinder that will allow it to be easily connected and disconnected.

72.3 *Powder Funnel*—The powder funnel allows for the addition of the reagents to the sample without interfering with the purged atmosphere in the vessel.

72.4 *Vent Tube*—The vent tube allows the escape of gas when reagents are being added through the powder funnel. If it is not present, reagents could be forced back through the powder funnel when they are added because the vessel is under positive pressure.

### 73. Reagents and Materials

73.1 *Hydrofluoric Acid/Hydrochloric Acid Mixture*—Mix 200 mL of hydrofluoric acid (HF) with 100 mL of 1 + 1 hydrochloric acid (HCl) and store in a polyethylene bottle. Degas the oxygen from the solution by bubbling with nitrogen, carbon dioxide, or argon for 1 h prior to use.

73.2 *Ascorbic Acid*.

73.3 *1,10 Phenanthroline Solution (0.5 %)*—Dissolve 2.5 g of 1,10 phenanthroline hydrochloride in 500 mL of deionized water.

73.4 *Sodium Acetate Solution (2 M)* (272 g of sodium acetate per litre)—Prepare 2 to 4 L at a time, filter if necessary, and store in a polyethylene bottle.

73.5 *Boric Acid, Saturated Solution*—Add 90 g of boric acid (H<sub>3</sub>BO<sub>3</sub>) to 1800 mL of deionized water.

73.6 *Iron Stock Solution (1 mL = 1 mg of iron)*—Weigh 3.5104 g of ferrous ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·6H<sub>2</sub>O) and transfer to a 500-mL volumetric flask. Dissolve in water, add 8 to 10 mL of concentrated HCl, dilute to volume, and mix.

73.7 *Dilute Iron Standard Solution (1 mL = 0.01 mg of iron)*—Pipet 10 mL of the iron stock solution into a 1-L volumetric flask, dilute to the mark with deionized water, and mix thoroughly.

73.8 *Nitrogen, Carbon Dioxide, or Argon Cylinder Gas*—The cylinder should be provided with a two-stage reducing valve and a gas-flow regulator for a flow rate of 28 to 280 L/h.

### 74. Procedure

74.1 Weigh or transfer 0.5000 g of powdered glass into a 400-mL plastic or TFE-fluorocarbon reaction vessel containing a small plastic-coated stir bar. Place the purging apparatus (see Fig. 2) into the vessel. Purge with carbon dioxide, nitrogen, or argon for 3 min. While continuing to purge, add 12 mL of the HF/HCl solution and begin stirring. Purge for 4 min. Add 200 mL of hot H<sub>3</sub>BO<sub>3</sub> solution (approximately 75°C) through the funnel and stir for 1 min additional. Add 50 mL of the sodium

acetate solution and stir for 1 min. Turn off the purge gas. Add 6 mL of the 1,10 phenanthroline solution and stir for 1 min. Note the time and make the absorbance reading 30 min. after addition of the 1,10 phenanthroline. Quantitatively transfer the solution to a 500-mL volumetric flask, cool to room temperature, and dilute to volume with deionized water that has been stored overnight to allow any bubbles to escape. Filter the solution through a medium porosity filter paper and measure the absorbance at 508 nm on the spectrophotometer.

### 75. Ferrous Iron Determination

75.1 Depending on the concentration of ferrous iron, measure the absorbance of the solution in either a 1 or 5-cm cell at 508 nm using a blank carried through the procedure as a reference.

75.2 *Calculation*—Convert the absorbance to micrograms of iron, using the calibration curve, and calculate the percent of FeO, *A*, as follows:

$$A = \frac{B \times 1.286 \times 100}{C \times 1\,000\,000} \times \frac{B \times 6.430 \times 10^{-4}}{C} \quad (26)$$

where:

*B* = weight of iron, µg, and

*C* = weight of sample, g.

### 76. Iron Standard Curve

76.1 Aliquot the diluted iron standard into a series of 100-mL beakers to cover the range from 0 to 150 µg. Add 0.5 g ascorbic acid and dilute to approximately 50 mL with deionized water. Neutralize to a pH of 2.5 to 3.0 using 2 M sodium acetate. Add 2 mL of the 1,10 phenanthroline solution. Quantitatively transfer the solutions into 100-mL volumetric flasks. Dilute to volume and mix thoroughly. Thirty minutes after adding the 1,10 phenanthroline, measure the absorbance in the 1 or 5-cm cells, as appropriate, at 508 nm using water as a reference. Plot the concentration (micrograms of iron) versus absorbance on linear graph paper or versus percent transmittance on semilog paper (percent transmittance on the log scale, concentration on the linear scale).

### 77. Keywords

77.1 chemical analysis; glass; referee analysis; routine analysis

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