



Designation: C169 – 16

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

This standard is issued under the fixed designation C169; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the U.S. 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 ( $P_2O_5$ ), 0.05 % zinc oxide (ZnO), 0.05 % antimony oxide ( $Sb_2O_3$ ), 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:

### Procedures for Referee Analysis:

	Sections
Silica	10
BaO, $F_2O_2$ ( $Al_2O_3 + P_2O_5$ ), CaO, and MgO	11 – 15
$Fe_2O_3$ , $TiO_2$ , $ZrO_2$ by Photometry and $Al_2O_3$ by Complexiometric Titration	16 – 22
$Cr_2O_3$ by Volumetric and Photometric Methods	23 – 25
MnO by the Periodate Oxidation Method	26 – 29
$Na_2O$ by the Zinc Uranyl Acetate Method and $K_2O$ by the Tetraphenylborate Method	30 – 33
$SO_3$ (Total Sulfur)	34 – 35
$As_2O_3$ by Volumetric Method	36 – 40

### Procedures for Routine Analysis:

Silica by the Single Dehydration Method	42 – 44
$Al_2O_3$ , CaO, and MgO by Complexiometric Titration, and BaO, $Na_2O$ , and $K_2O$ by Gravimetric Method	45 – 51
BaO, $Al_2O_3$ , CaO, and MgO by Atomic Absorption; and $Na_2O$ and $K_2O$ by Flame Emission Spectroscopy	52 – 59
$SO_3$ (Total Sulfur)	60
$B_2O_3$	61 – 62
Fluorine by Pyrohydrolysis Separation and Specific Ion Electrode Measurement	63 – 66
$P_2O_5$ by the Molybdo-Vanadate Method	67 – 70
Colorimetric Determination of Ferrous Iron Using 1,10 Phenanthroline	71 – 76

<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 Properties and Analysis.

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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>

- C146 Test Methods for Chemical Analysis of Glass Sand
- C225 Test Methods for Resistance of Glass Containers to Chemical Attack
- D1193 Specification for Reagent Water
- E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

## 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>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 **D1193**.

#### 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 **E60**.

<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 **C146** are equally applicable to these test methods.

#### 8. Preparation of Sample

8.1 Glass crushed in a steel mortar as described in Test Methods **C225**, 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.

Probable Precision of Results, weight %

Constituent	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
1 to 100	3
0.1 to 0.99	2
0.01 to 0.09	1 or 2
<0.01	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 be ignored. Thus, if the separation of BaO and the  $\text{H}_2\text{S}$

<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.

precipitation are bypassed, the analysis can begin with the ammonia precipitation of the  $R_2O_3$  group. Frequently, correction of the  $R_2O_3$  for  $Fe_2O_3$ , titanium dioxide ( $TiO_2$ ), and zirconium oxide ( $ZrO_2$ ) will allow a useful estimation of the remainder as aluminum oxide ( $Al_2O_3$ ); phosphoric anhydride ( $P_2O_5$ ) is usually small (less than 0.02 %). However, if chromic oxide ( $Cr_2O_3$ ) is present, it will be counted as  $Al_2O_3$ ; for example, in some green glasses,  $Cr_2O_3$  may be as much as 0.25 %.  $H_2SO_4$  is preferred to  $HClO_4$  in sample preparation when  $Cr_2O_3$  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  $HClO_4$  is used, whereas it is rendered insoluble with the use of  $H_2SO_4$ .

## 12. Determination of BaO

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

12.1.1 *Using  $HClO_4$* —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  $HClO_4$  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  $HClO_4$ . Cool, rinse down the sides of the dish, add 5 mL of saturated boric acid ( $H_3BO_3$ ) 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  $H_2S$  or  $NH_4OH$ .) Dilute to 100 mL and heat to a gentle boil. Precipitate barium by the slow addition of 10 mL of a 10 % solution of  $(NH_4)_2SO_4$  or 2 mL of  $H_2SO_4$  (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  $H_2SO_4$ . Reserve the filtrate (A). Proceed to 12.2.

12.1.2 *Using  $H_2SO_4$* —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  $H_2SO_4$  (1 + 1), and, if  $Cr_2O_3$  is present, 5 to 10 drops of  $H_2SO_3$  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  $H_2SO_4$ . Cool, rinse down the sides of the dish, add 2 mL of saturated  $H_3BO_3$  and 1 to 2 mL of  $HNO_3$ ; 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  $H_2S$  or  $NH_4OH$ .) When all sulfates have dissolved except barium, adjust the acidity by neutralizing with  $NH_4OH$  (using methyl red as the indicator) and reacidify with 1 mL of HCl. Add 3 to 4 drops of

$H_2SO_4$  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  $H_2SO_4$ . 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  $HClO_4$  or 5 to 6 mL of  $H_2SO_4$  (1 + 1) underneath the lid, return to the source of heat, and after all fluorides have reacted, and mild fuming of  $HClO_4$  or  $H_2SO_4$  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  $BaSO_4$  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  $Na_2CO_3$ , 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 %  $Na_2CO_3$  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  $NH_4OH$ , 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 ( $(NH_4)_2SO_4$ ) solution or 1 mL of  $H_2SO_4$  (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  $H_2SO_4$ . 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  $BaSO_4$ .

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

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

## 13. Determination of $R_2O_3$ by Ammonium Hydroxide Precipitation and Estimation of $Al_2O_3$ :

13.1 *Determination of  $R_2O_3$* :

13.1.1 Acidify the reserved  $Na_2CO_3$  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  $NH_4OH$ . Add about 3 to 5 mg of copper as  $CuCl_2$  (as a carrier), heat to near boiling, and precipitate by passing  $H_2S$  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  $H_2S$ . Discard the precipitate. Boil the solution to expel  $H_2S$ , add 3 to 4 mL of saturated bromine water, and boil to expel bromine.

13.1.2 Precipitate the  $R_2O_3$  by adding  $NH_4OH$  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  $\text{Fe}_2\text{O}_3$ , and so forth, 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 parachlorometaxylenol 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  $\text{Al}_2\text{O}_3$  and approximately 0.50 mL of CDTA or EDTA solution. Since the zinc solution is the standard for the  $\text{Al}_2\text{O}_3$  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  $\text{ZrO}_2$ )—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  $\text{ZrO}_2$ /mL. Transfer to a 1-L volumetric flask, dissolve in  $\text{HNO}_3$  (1 + 1), and dilute to volume with  $\text{HNO}_3$ (1 + 1).

17.20 *Zirconium Oxide, Dilute Standard Solution* (1 mL = 20  $\mu\text{g}$   $\text{ZrO}_2$ )—Dilute 100 mL of the 0.1 mg  $\text{ZrO}_2$ /mL standard solution to 500 mL in a volumetric flask with  $\text{HNO}_3$  (1 + 1).

## 18. Procedure

18.1 Grind clean pieces of sample in an agate mortar so that the coarsest pieces would pass a 150- $\mu\text{m}$  (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  $\text{HClO}_4$ . 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  $\text{HClO}_4$ . Cool, rinse down the sides of the dish, add 5 mL of saturated  $\text{H}_3\text{BO}_3$  solution, and evaporate to dryness. Eventually, partially cover the dish to remove the last traces of excess  $\text{HClO}_4$ . 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 ( $\text{BaSO}_4$ ). 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  $\text{Fe}_2\text{O}_3$ , 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  $\text{HClO}_4$  will oxidize Cr(III) to Cr(VI); hexavalent chromium will interfere in both the determination of  $\text{ZrO}_2$  and in the end point detection of the  $\text{Al}_2\text{O}_3$  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  $\text{SO}_2$ . 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  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ). 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  $\text{TiO}_2$ . 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 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  $\text{Fe}_2\text{O}_3$ , to a 100-mL volumetric flask. Dilute to about  $\frac{3}{4}$  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  $\text{Fe}_2\text{O}_3$  by reference to the standard curve, and calculate the percent of  $\text{Fe}_2\text{O}_3$  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 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 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>, and so forth (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:

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

If zinc back titer = 8.80 mL, then:

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

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 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  $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$  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  $\frac{1}{2}$  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 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  $\text{Cr}_2\text{O}_3$ /mL and 1  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_3$ /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 ( $\text{NaH}_2\text{PO}_4\text{-H}_2\text{O}$ ) 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  $\mu\text{g}$ .