



Designation: C 146 – 94a (Reapproved 1999)

Standard Test Methods for Chemical Analysis of Glass Sand¹

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1. Scope

1.1 These test methods cover the chemical analysis of glass sands. They are useful for either high-silica sands (99 % + silica (SiO_2)) or for high-alumina sands containing as much as 12 to 13 % alumina (Al_2O_3). Generally nonclassical, the test methods are rapid and accurate. They include the determination of silica and of total R_2O_3 (see 11.2.4), and the separate determination of total iron as iron oxide (Fe_2O_3), titania (TiO_2), chromium oxide (Cr_2O_3), zirconia (ZrO_2), and ignition loss. Included are procedures for the alkaline earths and alkalis. High-alumina sands may contain as much as 5 to 6 % total alkalis and alkaline earths. It is recommended that the alkalis be determined by flame photometry and the alkaline earths by absorption spectrophotometry.

1.2 These test methods, if followed in detail, will provide interlaboratory agreement of results.

NOTE 1—For additional information, see Test Methods C 169 and Practices E 50.

1.3 The test methods appear in the following order:

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1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

¹ These test methods are under the jurisdiction of ASTM Committee C-14 on Glass and Glass Products and are the direct responsibility of Subcommittee C14.02 on Chemical Properties and Analysis.

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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:

C 169 Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass²

C 429 Test Method for Sieve Analysis of Raw Materials for Glass Manufacture²

D 1193 Specification for Reagent Water³

E 11 Specification for Wire-Cloth Sieves for Testing Purposes⁴

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁵

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry⁵

2.2 Other Documents:

NIST Special Publication 260⁶

3. Significance and Use

3.1 These test methods can be used to ensure that the chemical composition of the glass sand meets the compositional specification required for this raw material.

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 used by means of a National Institute of Standards and Technology (NIST) standard reference material or other similar material of known composition 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*, current edition.

4. Photometers and Photometric Practice

4.1 Photometers and photometric practice prescribed in these test methods shall conform to Practice E 60.

² *Annual Book of ASTM Standards*, Vol 15.02.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

⁶ Standard samples available from the National Institute of Standards and Technology are listed in U.S. Dept. of Commerce, NIST, *Special Publication 260* (current edition), Washington, DC 20234.

5. Purity of Reagents

5.1 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.⁷ 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.

5.2 Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I, II, or III of Specification D 1193.

6. Concentration of Acids and Ammonium Hydroxide (NH₄OH)

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

	Sp Gr	%
Hydrochloric acid (HCl)	1.2	36 to 38
Hydrofluoric acid (HF)	1.2	48 to 51
Nitric acid (HNO ₃)	1.4	69 to 71
Perchloric acid (HClO ₄)	1.8	70 to 72
Sulfuric acid (H ₂ SO ₄)	1.8	95 to 98
Ammonium hydroxide (NH ₄ OH)	0.9	28 to 30

6.2 Concentrations of diluted acids and NH₄OH, 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 in the following example: HCl (1 + 99) means 1 volume of concentrated HCl (sp gr 1.19) added to 99 volumes of water.

7. Filter Papers

7.1 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.

8. Preparation of Sample

8.1 *General Considerations*—The acquisition and preparation of the sample shall follow the principles stated in Test Method C 429.

8.2 The laboratory sample is reduced for analysis to 10 to 20 g by use of a small riffle with openings preferably of 6.4-mm (1/4-in.) size. The analytical sample is then ground in an agate mortar to pass a 150- μ m (No. 100) sieve.⁸ If the laboratory sample as received contains any large particles that are retained

on a 850- μ m (No. 20) sieve, these shall be sieved out, crushed (without contamination) so as to pass the sieve, and then mixed back into the laboratory sample before riffing.

9. Precision and Bias

9.1 *Precision*—The probable precision of results that can be expected by the use of 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 the constituent present as well as the procedure used.

Constituent	Probable Precision of Results, Weight %	
	Referee Analysis	Routine Analysis
SiO ₂ (99 %)	±0.1	±0.25
SiO ₂ (85–90 %)	±0.1	±0.25
R ₂ O ₃ (1 %)	±0.05	±0.10
R ₂ O ₃ (10–15 %)	±0.1	±0.15
Al ₂ O ₃ (1 %)	±0.05	±0.10
Al ₂ O ₃ (10–15 %)	±0.1	±0.1
Fe ₂ O ₃	±0.003	...
TiO ₂	±0.005	...
ZrO ₂	±0.001 to 0.005	...
Cr ₂ O ₃	±0.0001 to 0.001	...
CaO	...	±0.001
MgO	...	±0.001
Na ₂ O	...	±0.001
K ₂ O	...	±0.001

9.2 *Bias*—Standard reference materials or other similar materials of known composition should be analyzed whenever possible to determine the bias of the results.

PROCEDURES FOR REFEREE ANALYSIS

10. Silica (SiO₂) by the Double Dehydration Method

10.1 Weigh 1.000 g of the powdered sample and 2.0 g of anhydrous sodium carbonate (Na₂CO₃) into a clean 75-mL platinum dish (Note 2); mix well with a platinum or Nichrome⁹ wire. Tap the charge so it lies evenly in the bottom of the dish. Cover evenly with an additional 1.0 g of Na₂CO₃. Cover with the 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.

NOTE 2—To obtain accurate repeat weighings, platinum ware must 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) 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

⁷ *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.

⁸ Requirements for sieves are given in ASTM Specification E 11.

⁹ Nichrome is a registered trademark of the Driver-Harris Co., 308 Middlesex St., Harrison, NJ 07029.

the cold HCl 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 glass¹⁰ during evaporation. When evaporation is complete (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.

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 SiO₂ as follows:

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

11. Total R₂O₃ by Ammonium Hydroxide (NH₄OH) Precipitation

11.1 *General Considerations*—The weight of sample taken for analysis is governed by the amount of Al₂O₃ known or suspected to be present. Sands low in Al₂O₃ (0.05 to 0.5 %) require a 5- to 10-g sample; sands with larger amounts of Al₂O₃ require a 0.5- to 1.0-g sample. Usually experience or prior information will indicate a satisfactory sample weight. The total R₂O₃ serves as a check on the sum of the R₂O₃ oxides determined separately. It also helps to identify an unknown sand as a low- or high-alumina type.

11.2 *Procedure*:

11.2.1 Weigh a suitable weight of sample into an 80- to 100-mL platinum dish, moisten, and add 10 mL of HF for each gram of sample taken; add 4 mL of H₂SO₄ (1 + 1) and evaporate to the first fuming of H₂SO₄ (Note 3). Cool, carefully wash down the sides of the dish with a minimum of water, and evaporate to the cessation of H₂SO₄ fumes. Cool, add 10 to 15 mL of HCl (1 + 1), 20 mL of hot water, and digest hot until the salts are in solution. If they do not dissolve readily, transfer to a beaker, police the dish, and boil the solution until the sulfates have dissolved (Note 4).

NOTE 3—Some sands may contain small amounts of organic matter as shown by the presence of carbon or carbonaceous material in the concentrated H₂SO₄. If this is the case, add 2 to 3 mL of HNO₃ and 10 to 15 drops of HClO₄, and proceed.

NOTE 4—High-alumina sands are generally mixtures of quartz and aluminum silicates of the feldspar group. Some of these silicates can contain barium. If a fine, white, insoluble precipitate persists, it is probably barium sulfate. In this case, partially neutralize the HCl until the solution is about 1 to 2 % acid, add about ten drops of H₂SO₄ (1 + 1) and boil gently for about 30 min. Cool, and after 1 to 2 h, filter the solution through a fine paper. The precipitate may be ignited and weighed and subsequently tested for barium. If the precipitate is not barium sulfate, it should be tested for silica. If the precipitate is neither of these, it can be considered R₂O₃ and added to the R₂O₃ found by ammonia precipitation.

11.2.2 If the expected R₂O₃ is about 10 mg, dilute the sample to about 75 to 100 mL; if much larger, dilute to about 200 to 250 mL. Add approximately 2 g of NH₄Cl, heat to boiling, add three to four drops of methyl red indicator solution and precipitate the R₂O₃ with the addition of NH₄OH (1 + 1). Add the NH₄OH slowly, stirring to obtain a sharp end point; finally add about four drops in excess for small amounts of precipitate and up to eight drops for large amounts. Boil the solution for about 2 min and filter through a coarse paper; there is no need to transfer quantitatively all the precipitate at this time. Wash the precipitate three to four times with hot 2 % NH₄Cl made neutral to methyl red. Transfer the precipitate back into the beaker and add 10 to 15 mL of HCl (1 + 1) and digest to disintegrate the paper and dissolve the precipitate. Dilute to approximately the same volume used for the first precipitation, reprecipitate with NH₄OH, and filter as before. Police the beaker with a bit of paper pulp to ensure complete recovery from the beaker. Wash four to five times with hot 2 % NH₄Cl solution.

11.2.3 Transfer the precipitate to a clean, tared platinum or porcelain crucible and ignite at a temperature of 1200°C for 30 min. Unglazed porcelain is best for the ignition as it does not change weight at this temperature. If platinum is used, both outer and inner surfaces should be polished bright. It is also advisable to carry an empty crucible through the ignition cycle to see if a platinum weight change occurs. A slight loss can be considered normal. If a gain in weight occurs, the platinum can be considered dirty and should be repolished and cleaned before reuse. The correct weight can be salvaged by brushing the dish or crucible free of precipitate and reweighing, in which case the original tare weight is not used for computation:

$$\text{R}_2\text{O}_3, \% = [(\text{weight of precipitate})/(\text{weight of sample})] \times 100 \quad (2)$$

11.2.4 The R₂O₃ contains the Al₂O₃, Fe₂O₃, TiO₂, ZrO₂, and Cr₂O₃ in the sample (phosphoric anhydride (P₂O₅) and vanadium pentoxide (V₂O₅) will be included if present, but this

¹⁰ A Fisher "Speedyvap," Catalog 2-609, available from Fischer Scientific Co., 585 Alpha Dr., Pittsburgh, PA 15238, has been found suitable for this purpose.

is not usual).¹¹ Al₂O₃ is estimated by subtracting the sum of the other oxides from the R₂O₃.

12. Preparation of the Sample for Determination of Iron Oxide, Titania, Alumina, and Zirconia

12.1 *Reagents: Fusion Mixture*—Weigh an approximate 1 + 1 mole portion of lithium carbonate (Li₂CO₃) and anhydrous sodium tetraborate (Na₂B₄O₇), 74 and 201 g, respectively, and mix intimately.

12.2 *Procedure for Low-Alumina, High-Silica Sands*—Weigh 4 g of sample dried at 110°C into a 75- to 100-mL platinum dish, add 40 mL of HF, and evaporate to near dryness. Wash down the sides of the dish with 10 mL of HF (use a small plastic cylinder or polyethylene dropping pipet) and evaporate to dryness (Note 5). Without any prior heating, evenly cover the residue in the dish with 2 ± 0.02 g of fusion mixture; heat over a gas burner until the residue is in solution in the melt (Note 6). To the fused residue, add 10 mL water and 20 mL of HClO₄(1 + 4); cover and digest hot until the melt is in solution (Note 7). Transfer to a 200-mL volumetric flask, cool, dilute to the mark, and mix (Note 8). The sample is now prepared for the determination of Fe₂O₃, Al₂O₃, TiO₂, and ZrO₂; the sample for Cr₂O₃ is prepared separately (see Section 17). Prepare a reagent blank with the samples. Aliquots identical to those for Fe₂O₃, TiO₂, and ZrO₂ are used as the photometric reference solutions (Note 9).

NOTE 5—In the procedure for high-alumina sands (12.3), it is preferable to add a few drops of H₂SO₄ with the second addition of HF. This eliminates the chance of volatilizing aluminum and titanium fluorides as the fusion is started.

NOTE 6—The fusion is rapid and can be performed simply as follows: Heat over a Meeker-type burner at a moderate heat until the mixture melts, apply just enough additional heat to give a moderate red heat. No lid is required if the initial heating is not too high. The fusion can be done in 2 min per sample. The dish must be handled with clean platinum-tipped tongs. The only allowable substitute is pure nickel tongs and these must be considered only in an emergency.

NOTE 7—Some samples may develop a cloudiness or precipitate after solution of the fusion or transfer to the volumetric flask. Tests have shown this will not affect results for Fe₂O₃, TiO₂, or Al₂O₃. After diluting to the mark of the flask and mixing, the precipitate is allowed to settle; sample aliquots are pipeted without disturbing the precipitate. The precipitate is probably a fluoborate.

NOTE 8—An aliquot of this solution can now be used for the Cr₂O₃ analysis (Section 17).

NOTE 9—Use of a predetermined amount of buffer for the determination of Fe₂O₃ and TiO₂ obviates the use of indicators and speeds the analysis when a group of samples must be analyzed. Preparation for this is made as follows: Weigh 2 g of fusion mix into a 250-mL beaker, add 100 mL of water and 20 mL of the HCl (1 + 4), cover, and boil for several minutes to eliminate CO₂. Cool and transfer to a 200-mL volumetric flask, dilute to the mark, and mix. Transfer a 25-mL aliquot to a 150-mL beaker and dilute to about 70 to 80 mL. Add from a 100-mL buret (which is used for dispensing) enough 2M sodium acetate solution to give a pH of 3.1 (make measurements with a pH meter). Record the volume used for the determination of iron. Continue adding sodium acetate until a pH of 3.8 is reached; record for the determination of titanium.

12.3 *Procedure for High-Alumina, Low-Silica Sands*—The method and technique is identical to 12.2 with the exception of

weights and volumes. Weigh 2 g of sample dried at 110°C into a 75-mL platinum dish and add 20 mL of HF; evaporate to near dryness. Wash down the sides of the dish with 5 mL of HF as in 12.2 and evaporate to dryness. Add 3 g of fusion mix and fuse as in 12.2. Add 15 mL of water and 26 mL of HCl (1 + 4) and digest until in solution. Transfer to a 100-mL volumetric flask; cool, dilute to the mark, and mix (Note 7). The amounts of predetermined buffer should be nearly the same as for 12.2; however, test the pH before proceeding (Note 8).

13. Iron Oxide (as Fe₂O₃) by the 1,10-Phenanthroline Method

13.1 Reagents:

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

13.1.2 *1,10-Phenanthroline*—The solution may be prepared from the monohydrate or the hydrochloride. The latter is readily water soluble; the monohydrate requires heating. Dissolve 12.0 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 13.0 g in 200 to 300 mL of water and dilute to 1 L; protect from light during storage. Two millilitres of either solution will complex 1.2 mg. This will cover the absorbance curve for the area of interest depending on instrumentation.

13.1.3 *Sodium Acetate (Buffer) Solution (2M)*—Dissolve 272 g of sodium acetate (CH₃COONa·3H₂O) 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.

13.2 Fe₂O₃ Procedure (For All Sands):

13.2.1 For sand with an iron content between 0.01 and 0.12 % Fe₂O₃, pipet an aliquot equivalent to 0.5 g (25 mL) into a 100-mL volumetric flask if the Fe₂O₃ is between 0.10 and 0.24 %, transfer the aliquot to a 200-mL volumetric flask (Note 10). If the Fe₂O₃ is higher than 0.24 %, a proportionally smaller aliquot will be necessary. By choice of volume and size of aliquots, a single standard curve should be adequate for the percentages of iron normally encountered in glass sand.

13.2.2 To the sample in the flask, add 1 mL of hydroxylamine hydrochloride and the predetermined amount of buffer, dilute to $\frac{3}{4}$ the volume of the flask, and add either 1 or 2 mL of 1,10-phenanthroline, depending on the iron present, mix, dilute to the mark, and after 5 min, measure the absorbance at 508 nm on a suitable (spectro) photometer. The reagent blank is used as the reference solution.

13.2.3 *Calculation*—Convert the photometric reading to milligrams of Fe₂O₃ by means of the standard curve, and calculate the percent Fe₂O₃ as follows:

$$\% \text{Fe}_2\text{O}_3 = \frac{A \times B \times 100}{C \times D \times 1000} \quad (3)$$

where:

- A = milligrams of Fe₂O₃ from the calibration curve;
- B = total volume from 12.2, mL;
- C = sample weight from 12.2, g; and

¹¹ Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, John Wiley and Sons, Inc., New York, 1938.

D = millilitres of aliquot from 13.2.1.

NOTE 10—If color is developed in a volumetric flask other than 100-mL volume, then this must be taken into account in the calculation in 13.2.3.

13.3 Preparation of the Standard Curve for Standard Iron Solution—Weigh 0.4911 g of ferrous ammonium sulfate into a 1-L volumetric flask, dissolve in water, add 8 to 10 mL of HCl, dilute to the mark and mix; 1 mL = 0.1 mg of Fe_2O_3 ; (the fact that the iron may slowly oxidize is of no consequence as it is subsequently reduced when developing the complex). Prepare a series of 100-mL volumetric flasks containing 0, 1, 2, 3, 4, 5, and 6 mL of the standard iron solution, dilute to 20 to 30 mL, and proceed as described in 13.2. The zero iron solution is the photometric reference. Plot on linear graph paper absorbance versus concentration in milligrams of Fe_2O_3 .

14. Titania (TiO_2) by the Tiron Method

14.1 Reagents:

14.1.1 *Buffer (2M Sodium Acetate)*—See 13.1.3.

14.1.2 *Acetate Buffer (pH 4.5)*—To 1 L of 1M sodium acetate solution add 390 mL of glacial acetic acid. Adjust to a pH of 4.5 with either solid sodium acetate or glacial acetic acid using a pH meter.

14.1.3 *Thioglycolic Acid (CH_2SHCOOH , Reagent, Assay 96 to 97 %)*—Prepare a 20 % v/v solution; keep refrigerated.

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

14.1.5 *Titanium Dioxide, Standard Solution (1 mL = 1.0-mg TiO_2)*—Weigh 1.0026 g of National Institute of Standards and Technology 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 percentage of TiO_2 .)

14.1.6 *Titanium Dioxide, Dilute Standard Solution (1 mL = 1.0-mg TiO_2)*—Pipet 50 mL of the 1.0-mg TiO_2 /mL standard solution into a 500-mL volumetric flask, add 15 mL of H_2SO_4 , and dilute to about 400 mL; mix by swirling. Cool to room temperature, if necessary; dilute to volume and mix.

14.2 TiO_2 Procedure (for All Sands):

14.2.1 Pipet an aliquot equal to 0.5 g of sample (25 mL) into a 50-mL volumetric flask for sand with TiO_2 between 0.005 to 0.05 % (Note 11), and add in order, with mixing, 1 mL of 20 % thioglycolic acid, 5 mL of Tiron reagent, the predetermined amount of 2M sodium acetate solution (to adjust the pH to approximately 4.5), and then 10 mL of the acetate buffer pH 4.5. Dilute to the mark, mix, and, after 15 min, measure the absorbance in 10 mm or comparable cells at 380 nm. The reagent blank is the reference solution.

NOTE 11—Samples suspected to contain more than 0.05 % TiO_2 should be pipeted into 100-mL volumetric flasks, or less sample and 2M sodium acetate buffer solution should be taken, or a combination of both. Since this reagent is about nine times as sensitive to titanium as peroxide, 0.25 mg of TiO_2 /50 mL or 0.5-mg/100-mL volume is the maximum that can be handled.

14.2.2 *Calculation*—Convert the photometric reading to milligrams of TiO_2 by means of the standard curve and calculate as for iron (see 13.2.3).

14.3 *Preparation of the Standard Curve for Standard Titanium Solution*—Prepare a series of 50-mL volumetric flasks containing 0.00, 0.05, 0.10, 0.15, 0.20, and 0.25 mg of TiO_2 and proceed as described in 14.2. The zero solution is the photometric reference. Plot concentration on linear graph paper. The absorbance for 0.3 mg of TiO_2 in 50-mL volume is about 1.150.

15. Alumina (Al_2O_3) by the CDTA Compleximetric Titration

15.1 Reagents:

15.1.1 *1,2-Cyclohexylene Dinitrilo Tetraacetic Acid (CDTA) Solution*—Dissolve 7.3 g of CDTA in 200 mL of water by the slow addition of 20 % w/v 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 Al_2O_3 .

15.1.2 *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_2O_3 and approximately 0.50 mL of CDTA solution. Since the zinc solution is the standard for the Al_2O_3 determination, it must be prepared with care and accuracy.

15.1.3 *Xylenol Orange Tetrasodium Salt (Indicator) Solution*—Dissolve 0.5 g in 100 mL of water and add one or two drops of HCl as stabilizer.

15.2 *Standardization of CDTA Solution with Standard Zinc Solution*—Accurately pipet 10 or 15 mL of CDTA solution into a 150- or 250-mL beaker and dilute to about 40 to 50 mL. Add 5 mL of 2M 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 12 in 15.3.4). 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 on at least two additional aliquots and average the titers. Millilitres of zinc solution divided by millilitres of CDTA equals millilitres of zinc equivalent of CDTA.

15.3 Al_2O_3 Procedure:

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

15.3.2 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 one or two 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.

15.3.3 *Calculation of Al₂O₃ and Correction for Fe₂O₃, TiO₂, and so forth (ZrO₂ and MnO₂, if determined)*—Calculate the net zinc titer by subtracting the zinc back titer from the millilitres zinc equivalent of CDTA used. Since the zinc solution equals 0.5-mg Al₂O₃/mL and 0.5 g of sample is titrated, calculate the uncorrected percentage of Al₂O₃ as follows:

$$\text{Al}_2\text{O}_3, \% \text{ (uncorrected)} = \text{net zinc titer} \times 0.1 \quad (4)$$

15.3.4 *Example*—If 15 mL of CDTA are added (estimated Al₂O₃ = 2.0 %), then:

$$\begin{aligned} 15 \times 2.02 \text{ (1-mL CDTA = 2.02-mL zinc solution)} \\ = 30.3\text{-mL zinc equivalent CDTA} \end{aligned} \quad (5)$$

$$\begin{aligned} \text{If zinc back titer} &= 8.80 \text{ mL, then} \\ (30.30 - 8.80) &= 21.50 \text{ mL} \\ &= 2.15 \% \text{ Al}_2\text{O}_3 \text{ uncorrected} \end{aligned} \quad (6)$$

To correct for Fe₂O₃ and TiO₂:

$$(\% \text{ Fe}_2\text{O}_3 + \% \text{ TiO}_2) \times 0.637 = \text{equivalent \% Al}_2\text{O}_3 \quad (7)$$

If % Fe₂O₃ = 0.045 and % TiO₂ = 0.018, then:

$$(0.045 + 0.018) = 0.063 \times 0.637 = 0.040 \quad (8)$$

$$2.15 - 0.040 = 2.11 \% \text{ Al}_2\text{O}_3 \text{ corrected for Fe}_2\text{O}_3 \text{ and TiO}_2 \quad (9)$$

ZrO₂ is corrected by multiplying % ZrO₂ × 0.413; and % MnO × 0.719. If determined, ZrO₂ and MnO equivalents are added to the correction for Fe₂O₃ and TiO₂ and the whole subtracted from percent uncorrected Al₂O₃.

NOTE 12—To provide a 5-mL excess of CDTA for complete complexation of aluminum, using a sample aliquot equal to 0.5 g, a sample containing 1.5 % Al₂O₃ will require 12.5 mL and a sample containing 3.0 % Al₂O₃, 20 mL, respectively. The pH of the sample solution may be adjusted to 5.3 by adding a predetermined amount of 2M 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 2M sodium acetate 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.

16. Zirconia (ZrO₂) by the Pyrocatechol Violet Method (for All Samples)

16.1 Reagents:

16.1.1 *Tri-n-Octyl-Phosphine Oxide (TOPO) Reagent*—Prepare an approximately 0.05M solution by dissolving 2 g of reagent in 100 mL of cyclohexane.

16.1.2 *Nitric Acid (7M)*—Approximately 7M acid is prepared by diluting one volume of HNO₃ (sp gr 1.42) with one volume of water.

16.1.3 *Pyrocatechol Violet*—Prepare a 0.15 % solution (weight/volume) in absolute ethyl alcohol by dissolving 37.5 mg of reagent in 25 mL of absolute ethyl alcohol. The solution must be prepared daily or just before use. The quality of pyrocatechol is always suspect and should be tested for sensitivity before use. This can be done by extracting a known quantity of ZrO₂, developing the complex as called for in 16.2, and comparing the actual absorbance with the expected absorbance. If it does not satisfactorily meet this level, it should be discarded.

16.1.4 *Ethyl Alcohol, Absolute*, 100 % or 200 proof reagent quality.

16.1.5 *Pyridine*, analytical reagent.

16.2 ZrO₂ Procedure (for All Samples):

16.2.1 Pipet an aliquot of the sample solution equal to 0.2 g (10 mL) into a 60-mL Squibb separatory funnel, preferably fitted with a TFE-fluorocarbon stopcock plug. Add 10 mL of HNO₃; and, if the solution has warmed significantly, cool to room temperature. Pipet 5 mL of TOPO-cyclohexane into the solution and extract zirconium by shaking or mixing for 10 min. Allow the liquid layers to separate, drain off the aqueous layer, and discard. Add 10 mL of 7M HNO₃, shake for 2 min; allow the layers to separate, drain, and reject the acid layer.

16.2.2 Transfer with a dry pipet 2 mL of the cyclohexane extract into a dry 25-mL volumetric flask. Add in order, while mixing, 10 mL of absolute alcohol, 1 mL of 0.15 % pyrocatechol violet, and 5 mL of pyridine. Finally, dilute to the mark of the flask with absolute alcohol and mix. Measure the absorbance in 10-mm cells at 655 nm. The reagent blank is the reference solution.

16.2.3 *Calculation*—Convert the photometric reading to micrograms of ZrO₂ by means of the standard curve and calculate percent ZrO₂ as follows:

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

where:

A = micrograms of ZrO₂,

B = grams of sample in sample aliquot, and

C = millilitres of TOPO aliquot per total millilitres of TOPO used.

Example: 20-μg ZrO₂ found in 2 mL of TOPO-cyclohexane extract of 10-mL sample aliquot:

$$\begin{aligned} 20/(0.2 \times 0.4) \times 10^{-4} &= 20/0.08 \times 10^{-4} \\ &= 250 \times 10^{-4} \\ &= 0.025 \% \text{ ZrO}_2 \end{aligned} \quad (11)$$

$$\begin{aligned} 0.2 &= \text{grams of sample in 10-mL aliquot} \\ 0.4 &= 2\text{-mL fraction of 5 mL} \\ &\text{of TOPO-cyclohexane extract} \end{aligned} \quad (12)$$

16.3 *Preparation of Standard Curve*—Standardize reagent quality zirconyl nitrate by careful ignition to the oxide as follows: 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 ZrO₂/mL. Transfer to a 1-L volumetric flask and dissolve in HNO₃ (1 + 2). This stock solution is relatively stable. A dilute standard equal to 0.01 mg/mL (10 μg/mL) is prepared from stock as needed; dilute with water. Prepare a series of solutions in 60-mL separatory funnels containing 0, 25, 50, 75, 100, and 125 μg of ZrO₂; dilute to at least 10 mL, then proceed as described in 16.2 for the determination of ZrO₂. Since 2-mL aliquots are 0.4 of the amount of ZrO₂ taken, the standard curve plot will represent, therefore, 10, 20, 30, 40, and 50 μg of ZrO₂ (Note 13). The zero solution is the reference. Plot on semilog paper, percent transmittance on the log scale, and concentration on the linear scale.

NOTE 13—The colored complex follows Beers' law up to a concentration of 60 μg/25 mL. The maximum amount of ZrO₂ that can be