



Standard Test Methods for Chemical Analysis of Glass Sand¹

This standard is issued under the fixed designation C146; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

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 C169 and Practices E50.

1.3 The test methods appear in the following order:

Procedures for Referee Analysis:	Section
Silica (SiO_2)—Double Dehydration	10
Total R_2O_3 —Gravimetric	11
Fe_2O_3 , TiO_2 , ZrO_2 , Cr_2O_3 , by Photometric Methods and Al_2O_3 by Compleximetric Titration	12 – 17
Preparation of the Sample for Determination of Iron Oxide, Titania, Alumina, and Zirconia	12
Iron Oxide (as Fe_2O_3) by 1,10-Phenanthroline Method	13
Titania (TiO_2) by the Tiron Method	14
Alumina (Al_2O_3) by the CDTA Titration Method	15
Zirconia (ZrO_2) by the Pyrocatechol Violet Method	16
Chromium Oxide (Cr_2O_3) by the 1,5-Diphenylcarbohydrazide Method	17
Procedures for Routine Analysis:	
Silica (SiO_2)—Single Dehydration	19
Al_2O_3 , CaO , and MgO —Atomic Absorption Spectrophotometry	20–25
Na_2O and K_2O —Flame Emission Spectrophotometry	26–27
Loss on Ignition (LOI)	28

¹ 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.

Current edition approved Oct. 1, 2014. Published October 2014. Originally approved in 1939. Last previous edition approved in 2009 as C146 – 94a (2009). DOI: 10.1520/C0146-94AR14.

1.4 *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:²

C169 Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass

C429 Test Method for Sieve Analysis of Raw Materials for Glass Manufacture

D1193 Specification for Reagent Water

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

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

2.2 Other Documents:

NIST Special Publication 260³

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.

² 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.

³ 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.

4. Photometers and Photometric Practice

4.1 Photometers and photometric practice prescribed in these test methods shall conform to Practice E60.

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.⁴ 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 D1193.

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 C429.

⁴ 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.

8.2 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-μm (No. 100) sieve.⁵ If the laboratory sample as received contains any large particles that are retained on a 850-μm (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 Nichrome⁶ 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

⁵ Requirements for sieves are given in ASTM Specification E11.

⁶ Nichrome is a registered trademark of the Driver-Harris Co., 308 Middlesex St., Harrison, NJ 07029.

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 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 glass 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 SiO_2 as follows:

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

11. Total R_2O_3 by Ammonium Hydroxide (NH_4OH) Precipitation

11.1 *General Considerations*—The weight of sample taken for analysis is governed by the amount of Al_2O_3 known or suspected to be present. Sands low in Al_2O_3 (0.05 to 0.5 %) require a 5- to 10-g sample; sands with larger amounts of Al_2O_3 require a 0.5- to 1.0-g sample. Usually experience or prior information will indicate a satisfactory sample weight. The total R_2O_3 serves as a check on the sum of the R_2O_3 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 H_2SO_4 (1 + 1) and evaporate to the first fuming of H_2SO_4 (Note 3). Cool, carefully wash down the sides of the dish with a minimum of water, and evaporate to the cessation of H_2SO_4 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 H_2SO_4 . If this is the case, add 2 to 3 mL of HNO_3 and 10 to 15 drops of HClO_4 , 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 H_2SO_4 (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 R_2O_3 and added to the R_2O_3 found by ammonia precipitation.

11.2.2 If the expected R_2O_3 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 NH_4Cl , heat to boiling, add three to four drops of methyl red indicator solution and precipitate the R_2O_3 with the addition of NH_4OH (1 + 1). Add the NH_4OH 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 % NH_4Cl 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 NH_4OH , 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 % NH_4Cl 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 R_2O_3 contains the Al_2O_3 , Fe_2O_3 , TiO_2 , ZrO_2 , and Cr_2O_3 in the sample (phosphoric anhydride (P_2O_5) and vanadium pentoxide (V_2O_5) will be included if present, but this is not usual).⁷ Al_2O_3 is estimated by subtracting the sum of the other oxides from the R_2O_3 .

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 (Li_2CO_3) and anhydrous sodium tetraborate ($Na_2 B_4O_7$), 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 $HClO_4$ (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 Fe_2O_3 , Al_2O_3 , TiO_2 , and ZrO_2 ; the sample for Cr_2O_3 is prepared separately (see Section 17). Prepare a reagent blank with the samples. Aliquots identical to those for Fe_2O_3 , TiO_2 , and ZrO_2 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 H_2SO_4 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 Fe_2O_3 , TiO_2 , or Al_2O_3 . After diluting to the mark of the flask and mixing, the precipitate is allowed to settle; sample aliquots are pipetted without disturbing the precipitate. The precipitate is probably a fluoborate.

NOTE 8—An aliquot of this solution can now be used for the Cr_2O_3 analysis (Section 17).

NOTE 9—Use of a predetermined amount of buffer for the determination of Fe_2O_3 and TiO_2 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 CO_2 . 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 Fe_2O_3) 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 ($CH_3COONa \cdot 3H_2O$) 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.

13.2 Fe_2O_3 Procedure (For All Sands):

13.2.1 For sand with an iron content between 0.01 and 0.12 % Fe_2O_3 , pipet an aliquot equivalent to 0.5 g (25 mL) into a 100-mL volumetric flask if the Fe_2O_3 is between 0.10 and 0.24 %, transfer the aliquot to a 200-mL volumetric flask (Note 10). If the Fe_2O_3 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 Fe_2O_3 by means of the standard curve, and calculate the percent Fe_2O_3 as follows:

$$\% Fe_2O_3 = \frac{A \times B \times 100}{C \times D \times 1000} \quad (3)$$

where:

A = milligrams of Fe_2O_3 from the calibration curve;

⁷ Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, John Wiley and Sons, Inc., New York, 1938.

- B** = total volume from 12.2, mL;
C = sample weight from 12.2, g; and
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 2 M 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 Al_2O_3 and Correction for Fe_2O_3 , TiO_2 , and so forth (ZrO_2 and MnO_2 , 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 Al_2O_3 /mL and 0.5 g of sample is titrated, calculate the uncorrected percentage of Al_2O_3 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 $\text{Al}_2\text{O}_3 = 2.0\%$), then:

$$15 \times 2.02 \text{ (1 - mL CDTA = 2.02 - mL zinc solution)} \quad (5)$$

$$= 30.3 - \text{mL zinc equivalent CDTA}$$

$$\text{If zinc back titer} = 8.80 \text{ mL, then} \quad (6)$$

$$(30.30 - 8.80) = 21.50 \text{ mL}$$

$$= 2.15\% \text{ Al}_2\text{O}_3 \text{ uncorrected}$$

To correct for Fe_2O_3 and TiO_2 :

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

If $\% \text{ Fe}_2\text{O}_3 = 0.045$ and $\% \text{ TiO}_2 = 0.018$, then:

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

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

ZrO_2 is corrected by multiplying $\% \text{ ZrO}_2 \times 0.413$; and $\% \text{ MnO} \times 0.719$. If determined, ZrO_2 and MnO equivalents are added to the correction for Fe_2O_3 and TiO_2 and the whole subtracted from percent uncorrected Al_2O_3 .

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 % Al_2O_3 will require 12.5 mL and a sample containing 3.0 % Al_2O_3 , 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 (ZrO_2) 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 HNO_3 (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 ZrO_2 , 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 ZrO_2 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 HNO_3 ; 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 7 M HNO_3 , 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 ZrO_2 by means of the standard curve and calculate percent ZrO_2 as follows:

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

where:

A = micrograms of ZrO_2 ,

B = grams of sample in sample aliquot, and

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

Example: 20- μg ZrO_2 found in 2 mL of TOPO-cyclohexane extract of 10-mL sample aliquot:

$$20/(0.2 \times 0.4) \times 10^{-4} = 20/0.08 \times 10^{-4} \quad (11)$$

$$= 250 \times 10^{-4}$$

$$= 0.025\% \text{ ZrO}_2$$

$$0.2 = \text{grams of sample in 10 - mL aliquot} \quad (12)$$

$$0.4 = 2 - \text{mL fraction of 5 mL}$$

$$\text{of TOPO - cyclohexane extract}$$

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 ZrO_2 /mL. Transfer to a 1-L volumetric flask and dissolve in HNO_3 (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 ZrO_2 ; dilute to at least 10 mL, then proceed as described in 16.2 for the determination of ZrO_2 . Since 2-mL aliquots are 0.4

of the amount of ZrO_2 taken, the standard curve plot will represent, therefore, 10, 20, 30, 40, and 50 μg of ZrO_2 (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 $\mu\text{g}/25$ mL. The maximum amount of ZrO_2 that can be completely extracted is about 125 to 150 μg . When more than 50 μg is found in the 2-mL aliquot taken for color development, a smaller aliquot should be taken and the procedure repeated.

Pressure may develop in the separatory funnel during extraction. After a minute or two of shaking, invert the funnel and carefully vent through the stopcock.

It is essential to use dry pipets and volumetric flasks as water will affect the intensity of the colored complex. Also, care must be taken not to get water into the pipet when taking aliquots from the separatory funnel.

17. Chromium Oxide (Cr_2O_3) by the 1,5-Diphenylcarbohydrazide Method

17.1 Reagents:

17.1.1 *1,5-Diphenylcarbohydrazide*—Dissolve 4 g of phthalic anhydride in 100 mL of ethyl alcohol by boiling under a reflux, cool, add 0.25 g of the reagent. Transfer to a glass-stoppered bottle, and store in a dark, cool place (a refrigerator is most satisfactory). So prepared, despite a slow yellow discoloration, the reagent is reasonably stable. However, it is advisable to test it with a standard chromate solution (10 or 20 μg) every three to four weeks.

17.1.2 *Fusion Mixture*—Same as for iron (12.1).

17.1.3 *Polyphosphate Solution* (approximate 10 % weight/volume for complexing iron)—Weigh 6.04 ± 0.02 g of sodium phosphate dibasic (Na_2HPO_4) and 5.87 ± 0.02 g of sodium phosphate monobasic ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) into a 100- or 125-mL platinum dish. (If a dish this large is not available, a smaller charge should be prepared.) Mix well and fuse by slowly raising the heat of a gas burner until the melt is a cherry-red and only a few bubbles remain. Remove the dish from the burner (platinum-tipped tongs) and rotate the melt to thin out the liquid layer of phosphate. When the melt has lost all color from heat, plunge it 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.

17.1.4 *Potassium Permanganate Solution*—A 0.3 % weight/volume solution in water.

17.1.5 *Sodium Azide Solution*—A 1 % weight/volume in solution in water.

17.2 Procedure:

17.2.1 Weigh 1 to 3 g of sample into a 75-mL platinum dish and add 10 mL of HF for each gram taken. If the sand is high in alumina (+10 %), restrict the sample size to 1 g. Add 2 mL of H_2SO_4 (1 + 1) and evaporate to incipient fumes of H_2SO_4 . Cool and wash down the sides of the dish with 10 mL of HF with the aid of a plastic dropper. Continue the evaporation to complete expulsion of H_2SO_4 . Some precaution will likely be necessary when attacking high-alumina sands. The reaction of the fluorides when converting to sulfates may cause considerable effervescence. In this case, cover about $\frac{7}{8}$ of the dish with a platinum lid (TFE-fluorocarbon is suitable), and continue

heating until the reaction is complete. Cool, rinse off the lid and down the sides of the dish, and evaporate to the expulsion of H_2SO_4 .

17.2.2 When evaporation is complete, weigh into the dish 1 g of $\text{Na}_2\text{CO}_3 \pm 0.02$ g and 1 g of fusion mixture ± 0.02 g (as used for iron), and mix the precipitate and fusion materials thoroughly with a glass rod. Fuse the sample over a gas burner or in a muffle furnace at a moderate temperature until the mass is clear, but do not prolong the time of fusion so as to avoid the loss of chromium.

NOTE 14—It is during the fusion of the residue that contamination is most likely to occur. Avoid chromium-containing triangles, tongs, and muffle furnaces with exposed metallic heating elements.

17.2.3 When the fusion is complete, cool the melt, add 10 mL of HClO_4 (1 + 1) and 10 to 15 mL of water; digest until solution is complete. Transfer to a 50-mL volumetric flask (the volume should not exceed 35 to 40 mL), add three to four drops of permanganate solution (enough to give a persistent color), and digest in boiling water for 30 to 40 min; all chromium will be oxidized to Cr^{+6} . Remove from the boiling water, add sodium azide solution dropwise at about 20-s intervals between drops. When the permanganate has been reduced, add 1 mL of polyphosphate solution and cool to room temperature. Add 2 mL of diphenylcarbohydrazide, dilute to the mark and mix, and measure percent transmittance on a spectrophotometer at 540 nm after 10 min but before 30 min from time of color development. For 1 to 15 μg of Cr_2O_3 , the preferred cell light path is 50 mm; for 15 to 70 μg , 10-mm cells are required. If the photometer cannot accommodate 50-mm cells, the largest for the available instrument should be used. The blank is the reference solution.

17.2.4 *Calculation*—Convert the photometric reading to micrograms of Cr_2O_3 by means of the appropriate standard curve and calculate percent Cr_2O_3 as follows:

$$\text{Cr}_2\text{O}_3, \% = (A/B) \times 10^{-4} \quad (13)$$

where:

- A = micrograms found in the sample solution,
- B = grams of sample represented by the sample solution, and
- 10 = 10^{-4} factor to convert 1 $\mu\text{g}/\text{g}$ of sample to percent.

17.3 Preparation of the Standard Curve:

17.3.1 *Standard Chromate Solutions*—Weigh 0.1935 g of $\text{K}_2\text{Cr}_2\text{O}_7$ or 0.2555 g of K_2CrO_4 into a 1-L volumetric flask and dilute to the mark; 1 mL = 0.1 mg/mL of Cr_2O_3 . Dilute 10 mL of this solution to 1 L in a volumetric flask to equal 1.0 μg of $\text{Cr}_2\text{O}_3/\text{mL}$; and 100 mL/L to equal 10.0 $\mu\text{g}/\text{mL}$.

17.3.2 *Perchloric Acid Solution* (1 + 4)—To 400 mL of water add 100 mL of 70 to 72 % HClO_4 and heat to about 60°C. Add dropwise sufficient N/10 permanganate solution to give a light pink color. Heat to near boiling until the permanganate has been reduced. Add more permanganate solution, dropwise, until a faint pink color appears. Continue to heat until this addition of permanganate solution also is reduced. Cool and store in a glass-stoppered borosilicate reagent bottle.

17.3.3 Prepare a series of 50-mL volumetric flasks to contain 0, 1, 3, 5, 7, 10, 12, and 15 μg of Cr_2O_3 as chromate and dilute to about 30 mL. Add 5 mL of perchloric acid

solution (1 + 4). Add 2 mL of diphenylcarbohydrazide, dilute to the mark of the flask and, after 10 min, measure percent transmission, in 50-mm absorbance cells, as described in the procedure for samples. The zero solution is the reference blank. Plot on semilog paper (percent transmittance on the log scale and concentration, in micrograms, on the linear scale). Prepare another series to contain 0, 10, 30, 50, 60, and 70 μg of Cr_2O_3 in 50-mL volumetric flasks, and proceed as for the first standard curve using 10-mm cells.

PROCEDURES FOR ROUTINE ANALYSIS

18. General Considerations

18.1 These procedures are designed for rapid, routine analysis. They are capable of producing results of satisfactory precision and accuracy. However, the proviso that “the analyst should check his procedures by the use of reference standards” is advised. Silica (SiO_2) is determined by a single dehydration method, with a colorimetric recovery of “soluble” silica. The Al_2O_3 , CaO , and MgO are determined using atomic absorption spectrophotometry while the Na_2O and K_2O are determined by flame emission spectrophotometry.

19. Silica (SiO_2) by the Single Dehydration Method

19.1 Reagents:

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

19.1.2 *Silicon Dioxide Standard Solution* (1 mL = 0.1-mg SiO_2)—Fuse 0.1000 g of pure anhydrous silicon dioxide (SiO_2) with 1 g of sodium carbonate (Na_2CO_3) in a covered platinum crucible or dish. Cool, dissolve completely in water, dilute to 1 L in a volumetric flask, and store immediately in a polyethylene bottle. It is recommended that pure quartz (99.9 % +) be used for preparation of the standard. Grind in an agate mortar to pass a 150- μm (No. 100) sieve and ignite at 1000 to 1200°C for 1 h. Store in a desiccator.

19.2 SiO_2 Procedure:

19.2.1 Weigh 1.000 g of powdered sample and 2.0 g of anhydrous sodium carbonate (Na_2CO_3) into a clean 75-mL platinum dish (Note 15); mix well with a platinum or Nichrome wire. Tap the charge so it lies evenly in the bottom of the dish. Cover evenly with an additional 1.0 g of Na_2CO_3 . Cover 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 15—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.

19.2.2 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 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 glass 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. However, catch the filtrate from the “first” dehydration in a 200-mL volumetric flask and reserve for the molybdate photometric recovery. Transfer the precipitate to the dish used for fusion and dehydration and determine weight of silica as described in 10.4. The weight of SiO_2 recovered by dehydration, $A = W_1 - W_2$.

19.2.3 Cool the filtrate to room temperature, dilute to volume, and mix. Transfer a 20-mL aliquot to a 50-mL volumetric flask and dilute to 30 to 35 mL. Add 10 mL of ammonium molybdate solution from a pipet, gently swirling the solution, dilute to volume, and mix. After 2 min, measure absorbance in 1-cm cells at 400 nm. Determine weight of SiO_2 recovered, B , by reference to the standard curve.

$$\text{Weight of SiO}_2, \text{ g} = \frac{\text{mg SiO}_2 \text{ (from curve)}}{20 - \text{mL (aliquot)}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \quad (14)$$

19.2.4 *Calculation*—Calculate the percent of SiO_2 as follows:

$$\text{SiO}_2, \% = [(A + B)/\text{wt of sample}] \times 100 \quad (15)$$

19.3 Preparation of Standard Curve:

19.3.1 Transfer 1.0, 2.0, 4.0, and 6.0 mL of SiO_2 standard solution (see 19.1.2) to 50-mL volumetric flasks containing 30 to 35 mL of water and 1.5 to 1.6 mL of HCl (1 + 1); mix by swirling. Add 10 mL of ammonium molybdate solution from a pipet, gently swirling the solution. Dilute to volume and mix. Prepare a reference solution with the above reagents but without silica.

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

19.3.3 *Standard Curve*—Plot the absorbance of the standard solutions versus tenths of a milligram of SiO_2 on linear coordinate graph paper.

20. Al_2O_3 , CaO , and MgO by Atomic Absorption; Na_2O and K_2O by Flame Emission Spectroscopy

20.1 Instrumentation:

20.1.1 *Atomic Absorption Spectrophotometers*—Commercially available instrumentation, using the laminar flow burner principle, has reached a satisfactory degree of performance and quality. Most instruments can be operated in both an absorbance and emission mode. The more sophisticated instrumentation also provides background and curve

correction and digital readout. Their most apparent weakness lies in imprecise gas flow regulation. Precision in readings and control of background can be improved by adding more precise controls to regulate pressure, flow, and fuel/oxidant ratios. The capability to precisely repeat burner height adjustments is not always adequate on some instruments.

20.2 The following features are considered essential for sand analysis:

20.2.1 Operation in both the absorbance and emission modes.

20.2.2 Chart recorder.

20.2.3 Noise suppression.

20.2.4 Variable slit.

20.2.5 Monochromater, minimum dispersion of 33 Å/mm.

20.2.6 Analytical sensitivity to the potassium 766-nm emission line, less than 0.1-ppm K_2O .

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

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

20.3.1 A 0.5-m focal length monochromater.

20.3.2 Maximum dispersion of 15 Å/mm or better.

20.3.3 Signal averaging.

20.3.4 Curve and background correction.

20.3.5 Digital readout.

20.3.6 Wavelength scanning drive.

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

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

21. Reagents

21.1 General Considerations:

21.1.1 Stock solutions for standards are prepared from appropriate reagent quality materials as chlorides. They are preferably stored in polyethylene bottles, although slightly acidic solutions stored in borosilicate chemical glassware

should be satisfactory. Appropriate dilutions are made as required for flame reference standards.

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

21.2 *Aluminum Oxide, Standard Solution* (1 mL = 0.5-mg Al_2O_3)—Dissolve 0.2647 g of spectroscopically pure aluminum metal in 12 mL of HCl (1 + 1) and dilute to 1 L. (If necessary, the addition of approximately 5 mg of mercuric chloride ($HgCl_2$) will hasten the solution of aluminum metal.) Further dilution of this results in 1 mL diluted to 1 L = 0.5-ppm Al_2O_3 .

21.3 *Calcium Oxide, Standard Stock Solution* (1 mL = 0.1-mg CaO)—Dissolve 0.1785 g of primary standard reagent grade calcium carbonate ($CaCO_3$), dried at 100°C, in 25 mL of HCl (1 + 4). Heat to a boil to remove CO_2 , cool, and dilute to 1 L.

21.4 *Calcium Oxide, Standard Solution* (1 mL = 0.01-mg CaO = 10 ppm)—Pipet 100 mL of the stock CaO solution into a 1-L volumetric flask and dilute to volume. Further dilution of this solution results in 10 mL diluted to 1 L = 0.1-ppm CaO.

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

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

21.7 *Potassium Oxide, Standard Stock Solution* (1 mL = 1-mg K_2O)—Dissolve 1.5829 g of potassium chloride (KCl), dried at 300°C, in 50 mL of water and 1 mL of HCl (1 + 1); dilute to 1 L.

21.8 *Potassium Oxide, Standard Solution* (1 mL = 0.1-mg K_2O = 100 ppm)—Pipet 100 mL of the stock K_2O solution into a 1-L volumetric flask and dilute to volume. Further dilution of this solution results in 2 mL diluted to 1 L = 0.2-ppm K_2O .

21.9 *Sodium Oxide, Standard Stock Solution* (1 mL = 1-mg Na_2O)—Dissolve 1.7101 g of sodium carbonate (Na_2CO_3), dried at 300°C, in 25 mL of water and 15 mL of HCl (1 + 4); heat to boiling to remove CO_2 , cool, and dilute to 1 L.

21.10 *Sodium Oxide, Standard Solution* (1 mL = 0.05-ppm Na_2O = 50 ppm)—Pipet 50 mL of the stock Na_2O solution into a 1-L volumetric flask and dilute to volume. Further dilution of this solution results in 20 mL diluted to 1 L = 1-ppm Na_2O ; 1.0 mL = 0.05-ppm Na_2O .

22. Flame Buffer Solutions

22.1 *Atomic Absorption (AA) Buffer Solution* (5 g of La_2O_3 , 20 mL of HCl, and 10 g of KCl per litre)—This solution should

be prepared in large quantities. It is used to dissolve and dilute samples prepared for the atomic absorption determination of Al_2O_3 , CaO , and MgO . For preparation of 10 L: Weigh 108.5 g of lanthanum chloride ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) (Note 16) and 100 g of potassium chloride (KCl) and transfer to a 1-L volumetric flask (preferably calibrated to deliver). Add about 500 mL of water and dissolve the salts. Add 200 mL of HCl , cool if necessary, and dilute to volume, or to the “to deliver” mark. Drain into a container that will hold 10 L (preferably of polyethylene). With the same flask, add nine more litres of water (Note 17). Thoroughly mix the solution. The container should be fitted with a siphon or spigot for dispensing the solution. When not in use, it must be sealed tightly to avoid evaporation loss.

NOTE 16—Lanthanum chloride reagent, even of the best purity, usually contains traces of calcium and lesser amounts of aluminum and magnesium as impurities. For this reason, it is advisable to prepare sufficient quantities of solutions from the same lot to accommodate a large number of determinations. It is also important to weigh the reagent and dispense solutions accurately so that standards and samples contain equal added concentrations of impurities which can be considered as “background.” Since a “bracketing” technique is used in comparing standards and sample, error is canceled. However, if the buffer solution used to prepare samples, and the lanthanum solution used to prepare the standards contribute different amounts of calcium, aluminum, or magnesium to the solutions prepared from them, the respective “backgrounds” will differ, and results can be in error. New lots of LaCl_3 should be checked for purity and, if necessary, new standards and buffer solutions prepared from the same lot.

NOTE 17—In keeping with the importance of obtaining samples and standards containing identical concentrations of lanthanum, accurate dilution of the buffer solution is necessary. Use of a flask calibrated “to deliver” is the most simple and best way to accomplish this. Error is about 0.5 mL/L. Conversely, the error for dispensing from a 2000-mL graduated cylinder may be 10 mL. For 10 L, this is 5 mL versus 50 mL, which is significant.

22.2 Lanthanum Chloride Solution for AA Standards (100-g $\text{La}_2\text{O}_3/\text{L}$)—This solution is used for the preparation of atomic absorption reference standards. For preparation of 2 L, weigh 434 g of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ and transfer to a 2-L volumetric flask. Dissolve in about 1 L of water, add 2 mL of HCl , and dilute to volume. 50 mL diluted to 1 L = 5-g $\text{La}_2\text{O}_3/\text{L}$.

22.3 Potassium Chloride Solution for AA Standards (200 g/L)—Prepare 2 L. Weigh 400 g of KCl and transfer to a 2-L volumetric flask. Dissolve in water and dilute to volume. Further dilution of this solution results in 50 mL diluted to 1 L = 10-g KCl/L .

22.4 Potassium Buffer Sodium Chloride Solution—This solution is used for the flame emission determination of K_2O . Dissolve 189 g of NaCl in water and dilute to volume in a 1-L volumetric flask. Ten millilitres diluted to 1 L equals a concentration of approximately 1000-ppm Na_2O .

22.5 Sodium Buffer Potassium Chloride Solution (159 g/L)—This solution is used for the flame emission determination of Na_2O . Dissolve 159 g of KCl in water and dilute to volume in a 1-L volumetric flask. 10 mL diluted to 1 L equals a concentration of approximately 1000-ppm K_2O .

23. Flame Spectrophotometry (Atomic Absorption and Emission)

23.1 General Considerations:

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

23.1.2 Table 2 outlines the equivalent concentration of the sample solution for each oxide; the normal range of each oxide as ppm in the sample solution and as weight percent in the sample itself (Note 18), and finally, the concentrations of reference standards to cover the normal range in steps for bracketing. The table is designed to cover most of the sands used in soda lime silica glasses. It can be used as a guide for sands whose composition may be outside the ranges noted; adjustment of sample size and dilution, and choice of reference standard concentration within instrument capability should enable a somewhat broader range of compositions to be determined.

NOTE 18—It is convenient to designate the reference samples in equivalent percent oxide as well as concentration in ppm. If the instrument is equipped with digital readout, absorbance, or emission usually can be adjusted to read directly in percent.

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

24. Flame Reference Standards

24.1 General Considerations—Reference standards are prepared by adding the appropriate buffer solutions, acid, and standards to provide the concentration ranges as outlined in Table 2. In practice, it is necessary to prepare only those known

TABLE 1 Parameters for Flame Spectrophotometry

Mode	Element	Oxidant/Fuel	Full-Scale Range, ppm		Base Solution		Analytical Line, nm
AA ^A	Al_2O_3	$\text{N}_2\text{O}/\text{A}$	5 to 50	0.5 % La	2 % HCl	1 % KCl	309
AA	CaO	$\text{N}_2\text{O}/\text{A}$	0.5 to 5	0.5 % La	2 % HCl	1 % KCl	422
AA	MgO	$\text{N}_2\text{O}/\text{A}$	0.1 to 2	0.5 % La	2 % HCl	1 % KCl	285
Fe^{B}	K_2O	air/A	0.1 to 2.0		2 % HCl	1000 ppm Na_2O	766 to 769
FE	Na_2O	air/A	0.1 to 2.0		2 % HCl	1000 ppm K_2O	589.2

^AAtomic absorption.

^BFlame emission.

TABLE 2 Concentrations of Sample and Reference Standards for Flame Spectrophotometry

	Sample Concentration Equivalent, g/L	Normal Range Oxide, ppm Sample Solution	Normal Range Oxide, Weight Percent in Sample	Concentration of Reference Standards, ppm
Al ₂ O ₃	5	2.5 to 50	0.05 to 1	2.0 to 50 in steps of 0.50 ppm
CaO	0.02	0.1 to 1	0.1 to 0.5	0.1, 0.5, 1.0
MgO (<1 %)	0.5	0.1 to 1	0.1 to 1	0.1, 0.5, 1.0
K ₂ O	0.4	0.2 to 2.0	0.05 to 0.5	0.2 to 2.0 in steps of 0.2 ppm
Na ₂ O	1.0	1.2 to 1.6	1.2 to 1.6	0.1 to 2 in steps of 0.05 ppm

to be needed. However, it is essential to have sufficient reference standards to bracket samples and establish the performance characteristics of the instrument.

24.2 Reference Standard Solutions for the Determination of Al₂O₃, by Atomic Absorption—Pipet into 1-L volumetric flasks 50 mL of LaCl₃ solution (100 g/L), 50 mL of KCl solution (200 g/L), 20 mL of HCl (added from a pipet or buret), and then the appropriate volume of the oxide standard solution to provide the required concentration. Dilute to volume and mix. Reference standards for Al₂O₃ are prepared from the 500-ppm standard solutions.

24.3 Reference Standard Solution for K₂O—Pipet, or add by a buret, into a 1-L volumetric flask containing about 200 mL of water, 10 mL of the potassium buffer NaCl solution (189 g/L), 20 mL of HCl, and then the appropriate volumes of the 100-ppm K₂O standard solution. Dilute to volume and mix.

24.4 Reference Standard Solution for Na₂O—Pipet, or add by a buret, into a 1-L volumetric flask containing about 200 mL of water, 10 mL of the sodium buffer KCl solution (159 g/L), 20 mL of HCl, and then the appropriate volumes of the 50-ppm Na₂O standard solution. Dilute to volume and mix.

25. Preparation of Sample Solutions for the Determination of Al₂O₃

25.1 Procedure:

25.1.1 Weigh 1.0000 g of sample into a 50- or 75-mL platinum dish, moisten with 2 mL of water, and add 3 mL of HF and 5 to 10 mL of HClO₄, while stirring with a platinum or plastic rod. Evaporate uncovered until fluorides begin to react, then cover with a platinum lid, allowing just sufficient space for HF to escape. When all reaction has subsided, cool, rinse off the lid and sides of the dish, stir, and evaporate to dryness. Cool slightly, rinse the sides of the dish with a minimum of water, add 3 to 4 mL of HClO₄, and again evaporate to dryness. It is essential to eliminate all traces of fluoride to avoid subsequent flame interference. Cool, dissolve the residue in about 20 mL of the atomic absorption (AA) buffer solution (22.1), and transfer to a 100-mL volumetric flask using buffer solution to rinse the platinum dish. Dilute to volume with the AA buffer solution.

25.1.2 For Determination of Al₂O₃—Transfer 25 mL of the sample solution to a 50-mL volumetric flask and dilute to volume with the AA buffer solution. This sample solution is suitable for the determination of Al₂O₃. Sample concentration = 5 g/L.

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

25.1.4 For Determination of MgO That is Less Than 1.0 %—Transfer 5 mL of the sample solution to a 100-mL volumetric flask and dilute to volume with AA buffer solution. Sample concentration = 0.5 g/L.

25.1.5 For Determination of MgO That is More Than 1.0 %—Use the sample solution prepared for the determination of CaO.

26. Preparation of Sample Solutions for the Determination of Na₂O and K₂O

26.1 Procedure:

26.1.1 Weigh 1.0000 g of sample into a 50- or 75-mL platinum dish, moisten with 1 mL of water, and add 2 to 3 mL of HF and 5 mL of HClO₄ while stirring with a platinum or plastic rod. Evaporate as described in 25.1.1; however, repeating the evaporation with additional HClO₄ is not necessary. Dissolve the dry residue in 10 to 15 mL of water and 2 mL of HCl. Transfer to a 100-mL volumetric flask. This solution is further diluted for the determination of Na₂O and K₂O.

26.1.2 For Determination of Na₂O—Transfer 10 mL of the sample solution to a 100-mL volumetric flask containing about 20 mL of water, add 1 mL of the sodium buffer KCl solution (159 g/L) and 2 mL of HCl from a buret. Dilute to volume and mix. Sample concentration = 1 g/L.

26.1.3 For Determination of K₂O—Transfer 10 mL of the sample solution to a 250-mL volumetric flask, add 25 mL of the potassium buffer NaCl solution (189 g/L), and 4.5 mL of HCl from a buret. Dilute to volume and mix. Sample concentration = 0.4 g/L.

27. Comparison of Samples to Reference Standards

27.1 Adjust the instrument to the proper operating parameters for the element oxide to be determined as recommended in the manufacturer's instructions. The instrument is operated in the absorption mode for the determination of Al₂O₃, CaO, and MgO, and in the emission mode for Na₂O and K₂O. When stability of response has been achieved, obtain at least three separate readings of the sample and of two reference standards that "bracket" the sample reading. Average the sample and standards readings and estimate the sample concentration by interpolation. The "bracketing" comparison technique should be observed regardless of how data are recorded: meter reading, chart recorder, or digital readout. The manufacturer's

instructions on handling data, background, and curve correction, if any, should be observed.

$$\text{Loss on ignition, \%} = (\text{loss/weight of sample}) \times 100 \quad (16)$$

28. Loss on Ignition

28.1 Weigh 1 to 3 g of the sample into a previously ignited (1000°C) tared crucible and ignite to constant weight at 1000°C. Cool in a desiccator and weigh.

29. Keywords

29.1 chemical analysis; glass sand; referee analysis; routine analysis

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; <http://www.copyright.com/>