



# Standard Test Methods for Chemical Analysis of Glass Sand<sup>1</sup>

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 ( $\epsilon$ ) 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 ( $\text{SiO}_2$ )) or for high-alumina sands containing as much as 12 to 13 % alumina ( $\text{Al}_2\text{O}_3$ ). Generally nonclassical, the test methods are rapid and accurate. They include the determination of silica and of total  $\text{R}_2\text{O}_3$  (see 11.2.4), and the separate determination of total iron as iron oxide ( $\text{Fe}_2\text{O}_3$ ), titania ( $\text{TiO}_2$ ), chromium oxide ( $\text{Cr}_2\text{O}_3$ ), zirconia ( $\text{ZrO}_2$ ), 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 ( $\text{SiO}_2$ )—Double Dehydration	10
Total $\text{R}_2\text{O}_3$ —Gravimetric	11
$\text{Fe}_2\text{O}_3$ , $\text{TiO}_2$ , $\text{ZrO}_2$ , $\text{Cr}_2\text{O}_3$ , by Photometric Methods and $\text{Al}_2\text{O}_3$ by Complexiometric Titration	12 – 17
Preparation of the Sample for Determination of Iron Oxide, Titania, Alumina, and Zirconia	12
Iron Oxide (as $\text{Fe}_2\text{O}_3$ ) by 1,10-Phenanthroline Method	13
Titania ( $\text{TiO}_2$ ) by the Tiron Method	14
Alumina ( $\text{Al}_2\text{O}_3$ ) by the CDTA Titration Method	15
Zirconia ( $\text{ZrO}_2$ ) by the Pyrocatechol Violet Method	16
Chromium Oxide ( $\text{Cr}_2\text{O}_3$ ) by the 1,5-Diphenylcarbohydrazide Method	17
Procedures for Routine Analysis:	
Silica ( $\text{SiO}_2$ )—Single Dehydration	19
$\text{Al}_2\text{O}_3$ , $\text{CaO}$ , and $\text{MgO}$ —Atomic Absorption Spectrophotometry	20–25
$\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$ —Flame Emission Spectrophotometry	26–27
Loss on Ignition (LOI)	28

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:<sup>2</sup>

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 260<sup>3</sup>

## 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.

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

<sup>3</sup> 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.

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

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#### 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.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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 (NH<sub>4</sub>OH)

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 <sub>3</sub> )	1.4	69 to 71
Perchloric acid (HClO <sub>4</sub> )	1.8	70 to 72
Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	1.8	95 to 98
Ammonium hydroxide (NH <sub>4</sub> OH)	0.9	28 to 30

6.2 Concentrations of diluted acids and NH<sub>4</sub>OH, except when standardized, are specified as a ratio stating the number of volumes of the concentrated reagent to be added to a given number of volumes of water, as 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.

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

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 (¼-in.) size. The analytical sample is then ground in an agate mortar to pass a 150-µm (No. 100) sieve.<sup>5</sup> 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 <sub>2</sub> (99 %)	±0.1	±0.25
SiO <sub>2</sub> (85–90 %)	±0.1	±0.25
R <sub>2</sub> O <sub>3</sub> (1 %)	±0.05	±0.10
R <sub>2</sub> O <sub>3</sub> (10–15 %)	±0.1	±0.15
Al <sub>2</sub> O <sub>3</sub> (1 %)	±0.05	±0.10
Al <sub>2</sub> O <sub>3</sub> (10–15 %)	±0.1	±0.1
Fe <sub>2</sub> O <sub>3</sub>	±0.003	...
TiO <sub>2</sub>	±0.005	...
ZrO <sub>2</sub>	±0.001 to 0.005	...
Cr <sub>2</sub> O <sub>3</sub>	±0.0001 to 0.001	...
CaO	...	±0.001
MgO	...	±0.001
Na <sub>2</sub> O	...	±0.001
K <sub>2</sub> 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 (SiO<sub>2</sub>) by the Double Dehydration Method

10.1 Weigh 1.000 g of the powdered sample and 2.0 g of anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) into a clean 75-mL platinum dish (Note 2); mix well with a platinum or Nichrome<sup>6</sup> wire. Tap the charge so it lies evenly in the bottom of the dish. Cover evenly with an additional 1.0 g of Na<sub>2</sub>CO<sub>3</sub>. 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

<sup>5</sup> Requirements for sieves are given in ASTM Specification E11.

<sup>6</sup> 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  $\text{SiO}_2$  as follows:

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

## 11. Total $\text{R}_2\text{O}_3$ by Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ) Precipitation

11.1 *General Considerations*—The weight of sample taken for analysis is governed by the amount of  $\text{Al}_2\text{O}_3$  known or suspected to be present. Sands low in  $\text{Al}_2\text{O}_3$  (0.05 to 0.5 %) require a 5- to 10-g sample; sands with larger amounts of  $\text{Al}_2\text{O}_3$  require a 0.5- to 1.0-g sample. Usually experience or prior information will indicate a satisfactory sample weight. The total  $\text{R}_2\text{O}_3$  serves as a check on the sum of the  $\text{R}_2\text{O}_3$  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  $\text{H}_2\text{SO}_4$  (1 + 1) and evaporate to the first fuming of  $\text{H}_2\text{SO}_4$  (Note 3). Cool, carefully wash down the sides of the dish with a minimum of water, and evaporate to the cessation of  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$ . If this is the case, add 2 to 3 mL of  $\text{HNO}_3$  and 10 to 15 drops of  $\text{HClO}_4$ , 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  $\text{H}_2\text{SO}_4$  (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  $\text{R}_2\text{O}_3$  and added to the  $\text{R}_2\text{O}_3$  found by ammonia precipitation.

11.2.2 If the expected  $\text{R}_2\text{O}_3$  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  $\text{NH}_4\text{Cl}$ , heat to boiling, add three to four drops of methyl red indicator solution and precipitate the  $\text{R}_2\text{O}_3$  with the addition of  $\text{NH}_4\text{OH}$  (1 + 1). Add the  $\text{NH}_4\text{OH}$  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 %  $\text{NH}_4\text{Cl}$  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  $\text{NH}_4\text{OH}$ , 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 %  $\text{NH}_4\text{Cl}$  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:

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