



# Standard Practices for Dissolving Glass Containing Radioactive and Mixed Waste for Chemical and Radiochemical Analysis<sup>1</sup>

This standard is issued under the fixed designation C 1463; 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 practices cover techniques suitable for dissolving glass samples that may contain nuclear wastes. These techniques used together or independently will produce solutions that can be analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), radiochemical methods and wet chemical techniques for major components, minor components and radionuclides.

1.2 One of the fusion practices and the microwave practice can be used in hot cells and shielded hoods after modification to meet local operational requirements.

1.3 The user of these practices must follow radiation protection guidelines in place for their specific laboratories.

1.4 Additional information relating to safety is included in the text.

1.5 The dissolution techniques described in these practices can be used for quality control of the feed materials and the product of plants vitrifying nuclear waste materials in glass.

1.6 These practices are introduced to provide the user with an alternative means to Test Methods C 169 for dissolution of waste containing glass in shielded facilities. Test Methods C 169 is not practical for use in such facilities and with radioactive materials.

1.7 The ICP-AES methods in Test Methods C 1109 and C 1111 can be used to analyze the dissolved sample with additional sample preparation as necessary and with matrix effect considerations. Additional information as to other analytical methods can be found in Test Method C 169.

1.8 Solutions from this practice may be suitable for analysis using ICP-MS after establishing laboratory performance criteria.

1.9 *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.* Specific precautionary statements are given in Section 18.

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 169 Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass<sup>2</sup>

C 1109 Test Method for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectrometry<sup>3</sup>

C 1111 Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectrometry<sup>3</sup>

C 1220 Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste<sup>3</sup>

C 1285 Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)<sup>3</sup>

D 1193 Specifications for Reagent Water<sup>4</sup>

## 3. Summary of Practice

3.1 The three practices for dissolving silicate matrix samples each require the sample to be dried and ground to a fine powder.

3.2 In the first practice, a mixture of sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is mixed with the sample and fused in a muffle for 25 min at 950°C. The sample is cooled, dissolved in hydrochloric acid, and diluted to appropriate volume for analyses.

3.3 The second practice described in this standard involves fusion of the sample with potassium hydroxide (KOH) or sodium peroxide ( $\text{Na}_2\text{O}_2$ ) using an electric bunsen burner, dissolving the fused sample in water and dilute HCl, and making to volume for analysis.

3.4 Dissolution of the sample using a microwave oven is described in the third practice. The ground sample is digested in a microwave oven using a mixture of hydrofluoric (HF) and nitric ( $\text{HNO}_3$ ) acids. Boric acid is added to the resulting solution to complex excess fluoride ions.

3.5 These three practices offer alternative dissolution methods for a total analysis of a glass sample for major, minor, and

<sup>1</sup> These practices are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.05 on Analytical Test Methods.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 15.02.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

radionuclide components.

#### 4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.<sup>5</sup>

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean at least Type II reagent water in conformance with Specification D 1193.

### PRACTICE 1—FUSION WITH SODIUM TETRABORATE AND SODIUM CARBONATE

#### 5. Scope

5.1 This practice covers flux fusion sample decomposition and dissolution for the determination of SiO<sub>2</sub> and many other oxides in glasses, ceramics, and raw materials. The solutions are analyzed by atomic spectroscopy methods. Analyte concentrations ranging from trace to major levels can be measured in these solutions, depending on the sample weights and dilution volumes used during preparation.

#### 6. Technical Precautions

6.1 This procedure is not useful for the determination of boron or sodium since these elements are contained in the flux material.

6.2 The user is cautioned that with analysis by ICP-AES, AAS, and ICP-MS, the high sodium concentrations from the flux may cause interferences.

6.3 Elements that form volatile species under these alkaline fusion conditions may be lost during the fusion process (that is, As and Sb).

#### 7. Apparatus

7.1 *Platinum Crucibles*, 30 mL.

7.2 *Balance*, analytical type, precision to 0.1 mg.

7.3 *Furnace*, with heating capacity to 1000°C.

7.4 *Crucible Tongs*, (cannot be made of iron, unless using platinum-clad tips).

7.5 *Polytetrafluoroethylene (PTFE) Beaker*, 125-mL capacity.

7.6 *Magnetic Stir Bar*, PTFE-coated (0.32 to 0.64 cm).

7.7 *Magnetic Stirrer*.

7.8 *Mortar and Pestle*, agate or alumina (or equivalent grinding apparatus).

7.9 *Sieves*, 100 mesh.

#### 8. Reagents and Materials

8.1 *Anhydrous Sodium Carbonate* (Na<sub>2</sub>CO<sub>3</sub>).

8.2 *Anhydrous Sodium Tetraborate* (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>).

8.3 *Sodium Nitrate* (NaNO<sub>3</sub>).

8.4 *Hydrochloric Acid* (HCl), 50 % (v/v), made from concentrated hydrochloric acid (sp gr 1.19) and water.

8.5 *Nitric Acid* (HNO<sub>3</sub>), 50 % (v/v), made from concentrated nitric acid (sp gr 1.44) and water.

#### 9. Hazards and Precautions

9.1 Follow established laboratory practices when conducting this procedure.

9.2 The operator should wear suitable protective gear when handling chemicals.

9.3 The dilution of concentrated acids is conducted in fume hoods by cautiously adding an equal part acid to an equal part of deionized water slowly and with constant stirring.

9.4 Samples that are known or suspected to contain radioactive materials must be handled with the appropriate radiation control and protection as prescribed by site health physics and radiation protection policies.

9.5 Samples that are known or suspected to contain toxic, hazardous, or radioactive materials must be handled to minimize or eliminate employee exposure. Fusion and leaching of the fused samples must be performed in a fume hood, radiation-shielded facility, or other appropriate containment.

#### 10. Sample Preparation

10.1 If the material to be analyzed is not in powder form, it should first be broken into small pieces by placing the sample in a plastic bag and then striking the sample with a hammer. The sample should then be ground to pass a 100-mesh sieve using a clean mortar and pestle such as agate or alumina

#### 11. Procedure

11.1 Weigh 50 to 250 mg of a powdered sample into a platinum crucible on an analytical balance to ± 0.1 mg. The sample size is dependent on the analyte concentration.

NOTE 1—Although the larger sample size has generally worked well, some matrices may not dissolve entirely. Try smaller sample sizes if that is the case.

11.2 Add 0.5 ± 0.005 g each of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> to the crucible containing the sample.

11.3 Stir the sample/flux mixture in the crucible with a spatula until a mixture is obtained. Prepare a reagent blank.

11.4 For samples containing minor to major elements that do not oxidize readily (such as Pb, Fe, etc.), add 300 mg of sodium nitrate. If desired, a Pt lid can be placed on the crucible to reduce splattering. When adding nitrate, 50 % v/v HNO<sub>3</sub> should be the diluting acid in order to reduce the attack on platinum in 11.6.

11.5 Using the crucible tongs, place the crucible containing the sample/flux mixture into a muffle furnace for 25 min at a temperature of 950°C. Remove the crucible from the furnace and allow the melt to cool to room temperature.

11.6 Place a stir bar in each crucible and add 4 mL 50 % v/v HCl, and then dilute with H<sub>2</sub>O to near the top of the crucible.

NOTE 2—In some cases, 50 % v/v HNO<sub>3</sub> may be more appropriate than HCl (that is, samples for ICP-MS, high lead samples, or when sodium nitrate was added).

11.7 Place the crucible on the magnetic stirrer, and stir until the sample melt is dissolved completely (approximately 30

<sup>5</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. Pharmacopeia Convention, Inc. (USPC), Rockville, MD.

min). If undissolved material remains, the fusions described in Section 20 may need to be tried for cross correlation.

11.8 To a calibrated volumetric flask, typically 100, 250, 500, or 1000 mL, add enough 1:1 HCl to make the final concentration 2 % (including the acid already in the crucible). The final volume is determined by the expected analyte concentrations. Quantitatively transfer the sample solution, and dilute.

11.9 The dilution volume is determined by the user of the practice and is dependent upon the desired analysis.

11.10 See Appendix X1 for examples of analytical data using solutions from this fusion.

## PRACTICE 2—FUSION WITH POTASSIUM HYDROXIDE OR SODIUM PEROXIDE

### 12. Scope

12.1 This practice covers alkaline fusion of silicate matrix samples (or other matrices difficult to dissolve in acids) using an electric Bunsen burner mounted on an orbital shaker. This practice has been used successfully to dissolve borosilicate glass, dried glass melter feeds, various simulated nuclear waste forms, and dried soil samples.

12.2 This fusion apparatus and the alkaline fluxes described are suitable for use in shielded radiation containment facilities such as hot cells and shielded hoods.

12.3 When samples dissolved using this practice are radioactive, the user must follow radiation protection guidelines in place for such materials.

### 13. Summary of Practice

13.1 An aliquot of the dried and ignited sample is weighed into a tared nickel or zirconium metal crucible and an appropriate amount of alkaline flux (potassium hydroxide or sodium peroxide) is added. The crucible is placed on a preheated electric Bunsen burner (1000°C capability) mounted on an orbital shaker. The speed of the shaker is adjusted so that the liquefied alkali metal flux and the sample are completely fused at the bottom of the crucible. When the fusion is complete (about 5 min), the crucible is removed from the heater and cooled to room temperature. The fused mixture is dissolved in water, acidified with hydrochloric acid, and diluted to an appropriate volume for subsequent analysis.

13.2 With appropriate sample preparation, the solution resulting from this procedure can be analyzed for trace metals by ICP-AES, ICP-MS, and AAS, and for radionuclides using applicable radiochemical methods.

### 14. Significance and Use

14.1 This practice describes a method to fuse and dissolve silicate and refractory matrix samples for subsequent analysis for trace metals and radionuclides. These samples may contain high-level radioactive nuclear waste. Nuclear waste glass vitrification plant feeds and product can be characterized using this dissolution method followed by the appropriate analysis of the resulting solutions. Other matrices such as soil and sediment samples and geological samples may be totally dissolved using this practice.

14.2 This practice has been used to analyze round-robin simulated nuclear waste glass samples.

14.3 This practice can be used for bulk analysis of glass samples for the product consistency test (PCT) as described in Test Methods C 1285 and for the analysis of monolithic radioactive waste glass used in the static leach test as described in Test Method C 1220.

14.4 This practice can be used to dissolve the glass reference and testing materials described in Refs (1) and (2).<sup>6</sup>

### 15. Interferences

15.1 Elements that form volatile species under these alkaline fusion conditions will be lost during the fusion process.

15.2 The high alkali metal (Na or K) content of the resulting sample solutions can cause interference with ICP nebulizer and torch assemblies due to salt deposition. Dilution of the sample solutions may be necessary.

15.3 The metallic impurities, that is, Na, K, in the alkaline flux used to fuse the samples can cause a positive bias if proper corrections are not applied. Method blanks must be determined to allow correction for flux impurity concentration.

### 16. Apparatus

16.1 *Analytical Balance*, capable of weighing to  $\pm 0.1$  mg.

16.2 *Electric Bunsen Burner*, capable of heating to 1000°C.<sup>7</sup> to accommodate the larger size (100 mL nickel) metal crucibles, the heat shield on top of the electric Bunsen Burner is wrapped with a noncorrosive wire such as iniconel at three evenly distributed locations. With the wire on the heat shield, the large size crucibles are better supported and more easily removed. A wire basket made from the noncorrosive wire is also fabricated so that smaller size crucibles (55 mL zirconium) that pass through the heat shield are supported evenly in the heating mandrel of the electric Bunsen burner. Fig. 1 shows the electric Bunsen burner mounted on the orbital shaker with the above modifications for crucible mounting.

16.3 *Orbital Shaker*, including a holder fabricated to fasten the electric Bunsen burner on the platform (see Fig. 1).<sup>8</sup>

16.4 *Manual Adjustable Power Supply*, for controlling the temperature of the electric Bunsen burner.<sup>9</sup>

16.5 *Zirconium Metal Crucible*, 55 mL capacity, high form. Different shape and capacity crucibles also may be used when necessary.

16.6 *Nickel Metal Crucible*, 100 mL capacity, high form. Different shape and capacity crucibles also may be used when necessary.

16.7 *Aluminum Oxide Crucible*, 55 mL capacity. Different shape and capacity may be used depending upon sample sizes taken.

16.8 *200 Mesh (74  $\mu$ m) Sieve*.

16.9 *Hot Plate or Steam Bath*, capable of heating to 100°C.

### 17. Reagents and Materials

17.1 *Purity of Reagents*—All chemicals used in this practice

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this practice.

<sup>7</sup> Electric bunsen burners are available from most major laboratory supply houses.

<sup>8</sup> Orbital shaker, Model 04732-00 available from Cole-Parmer Instrument Company, has been found to be suitable for this purpose.

<sup>9</sup> The Model 01575-26 power supply available from Cole-Parmer Instrument Company has been found to be suitable for this purpose.





FIG. 1 Electric Bunsen Burner Mounted on the Orbital Shaker

are to be reagent grade. Unless otherwise indicated all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.<sup>5</sup>

17.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean at least Type II reagent water conforming to Specification D 1193.

17.3 *Potassium Hydroxide* (KOH), pellet.

17.4 *Potassium Nitrate* (KNO<sub>3</sub>), crystal.

17.5 *Sodium Peroxide* (Na<sub>2</sub>O<sub>2</sub>), granular.

17.6 *Hydrochloric Acid* (HCl), concentrated, sp gr 1.19.

17.7 *Nitric Acid Solution* (2 vol %)—Add 20 mL of concentrated nitric acid (HNO<sub>3</sub>, sp gr 1.42) to 950 mL of water while stirring. Make to 1 L volume and store in a polyethylene bottle.

17.8 *Oxalic Acid*, crystals.

## 18. Hazards and Precautions

18.1 Samples that are known or suspected to contain radioactive materials must be handled with the appropriate radiation control and protection as prescribed by site health physics and radiation protection policies.

18.2 Samples that are known or suspected to contain toxic, hazardous, or radioactive materials must be handled to minimize or eliminate employee exposure. Fusion and leaching of the fused samples must be performed in a fume hood, radiation-shielded facility, or other appropriate containment. Personal protective equipment must be worn when appropriate. All site good laboratory safety and industrial hygiene practices must be followed.

18.3 Sodium peroxide is a strong oxidizer. Precaution must be taken when fusions are performed on samples containing materials that are readily oxidized.

18.4 Samples containing significant concentrations of phosphates (greater than 5 %) cannot be fused in a zirconium metal

crucible using sodium peroxide. The phosphate destroys the oxide layer on the crucible, resulting in severe corrosion. Aluminum oxide crucibles can be substituted for fusion of samples containing phosphates greater than 5 %.

## 19. Sample Preparation

19.1 *Wet or Slurry Samples:*

19.1.1 Dry wet or slurry samples in a tared porcelain crucible at 105°C. Grind the dried sample in a porcelain mortar to a particle size to pass a No. 200 (74 μm) sieve.

19.1.2 Weigh a portion (approximately 3 g) of the dried and ground sample described in 19.1.1 to the nearest 0.001 g in a tared porcelain crucible. Ignite the sample at 1000°C and determine the sample loss on ignition factor ( $I_F$ ), where:

$$I_F = (W_i - W_f) / (W_i) \quad (1)$$

where:

$W_i$  = initial sample weight, and

$W_f$  = sample weight after ignition.

19.2 *Dry Solid or Oxide Samples:*

19.2.1 Grind the dry solid or oxide sample to a particle size to pass a No. 200 (74 μm) sieve.

19.2.2 Weigh a portion (approximately 3 g) of the ground sample described in 19.2.1 to the nearest 0.001 g in a tared porcelain crucible. Ignite the sample at 1000°C and determine the ignition factor in accordance with equation 19.1.2

NOTE 3—The loss on ignition for dry solid or oxide samples may be negligible.

## 20. Procedure

20.1 *Potassium Hydroxide Fusion*—The KOH fusion is performed in a nickel metal crucible.

20.1.1 The choice of fusion methods described in 20.1 and 20.2 is determined by the analyte elements to be determined;

that is, if combinations of Na, K, Ni, or Zr are to be determined, then one or both of the fusion methods may have to be performed.

20.1.2 Set the manually adjustable power controller that supplies power to the electric Bunsen burner so that 1.6 g of NaOH in a zirconium crucible will melt within 1 to 2 min.

20.1.3 Tare a nickel metal crucible to the nearest 0.001 g.

20.1.4 Weigh an aliquot of the ground sample described in 19.1.1 or 19.2.1, which is equivalent to  $0.350 \pm 0.050$  g of ignited sample (19.1.2 or 19.2.2). Determine the amount of dried sample ( $W_s$ ) to be aliquoted by using the ignition factor from 19.1.2 as follows:

$$W_s = (0.350 \text{ g}) / (1 - I_F) \quad (2)$$

20.1.5 Add  $1.600 \pm 0.200$  g of KOH pellets. Record the weight of KOH added to the crucible to the nearest 0.001 g. Swirl the crucible to mix the sample and the KOH pellets completely.

20.1.6 Reagent grade KOH will contain trace amounts of sodium as an impurity. A correction for this flux impurity should be made to the sodium found in the sample.

20.1.7 Set the crucible on the preheated electric Bunsen burner and turn on the orbital shaker.

20.1.8 Fuse the sample mixture for approximately 5 min or until the fusion is complete. If at the completion of the fusion or after about 5 min of heating, there is still undissolved material, remove the crucible from the burner, allow to cool, and add 0.5 mL of water. Replace the crucible on the burner and continue fusion until dissolution is complete.

NOTE 4—During the KOH fusion, the flux will become more viscous as the fusion continues. If the temperature of the electric Bunsen burner is set too high, the KOH will solidify before the fusion is complete. Once the fusion mixture has solidified and the heating is continued, further dissolution of the sample ceases and some of the dissolved silicates in the sample will dehydrate, resulting in incomplete dissolution of the fused sample.

20.1.9 When fusion is complete, remove the crucible from the burner and allow to cool to room temperature.

20.1.10 Add water drop-wise to the crucible until the initial vigorous reaction subsides. Add a total of about 10 mL of water to dissolve the fused mixture. Transfer the solution to a 250-mL volumetric flask. If the initial dissolution was not complete, continue to add water until all the fused sample has been dissolved and then transfer the resulting solution to the flask.

20.1.11 Add 50 mL of 1 + 1 HCl and 0.5 g of oxalic acid to the volumetric flask. Dilute with water until the volume in the flask is about 150 mL. If the solution is still cloudy (white precipitate), heat the flask carefully on a hot plate to near boiling. Continue to heat without boiling until the precipitate dissolves. Cool the flask to room temperature and make the solution to volume with water. Mix the solution thoroughly.

NOTE 5—Oxalate in an acidic solution will dissolve zirconium phosphate. Heating accelerates the dissolution rate. If dehydrated silicic acid was produced during the fusion, this material will not dissolve and the fusion process (20.1.8) will need to be repeated.

20.1.12 A ten-fold dilution of this solution in 2 % nitric acid is necessary for ICP-AES or AAS analysis for metals.

20.2 *Sodium Peroxide Fusion*—The  $\text{Na}_2\text{O}_2$  fusion is performed in a zirconium metal crucible.

20.2.1 Set the adjustable power controller on the electric Bunsen burner so that 1.6 g of  $\text{Na}_2\text{O}_2$  in a zirconium crucible will melt in 1 to 2 min. This is the same setting determined in 20.1.2.

20.2.2 Tare a zirconium crucible to within 0.001 g.

20.2.3 Weigh an aliquot of the ground sample described in 19.1.1 or 19.2.2, which is equivalent to  $0.350 \pm 0.050$  g of ignited sample. Use the equation in 20.1.4 to calculate the aliquot of the dried sample to fuse.

20.2.4 Add  $1.600 \pm 0.2$  g of granular  $\text{Na}_2\text{O}_2$ . Record the weight of  $\text{Na}_2\text{O}_2$  added to the nearest 0.001 g. Swirl the crucible to completely mix the sample into the  $\text{Na}_2\text{O}_2$  granules.

20.2.5 Set the crucible on the preheated electric Bunsen burner and turn on the orbital shaker. Fuse the mixture for approximately 5 min or until fusion is complete.

20.2.6 Remove the crucible from the burner and cool to room temperature.

20.2.7 Add water drop-wise until the initial vigorous reaction subsides. Add about 10 mL of water to dissolve the fusion mixture. Transfer the solution to a 250-mL volumetric flask. If the initial dissolution was not complete, continue to add water, and add the solution to the flask.

20.2.8 Add 50 mL of 1 + 1 HCl and 0.5 g of oxalic acid to the volumetric flask. Dilute with water until the volume in the flask is about 150 mL. If the solution is cloudy (white precipitate) heat the flask on a hot plate to near boiling while taking care to avoid solution bumping. Continue careful heating the flask without boiling until the precipitate dissolves. Refer to Note 5 if the precipitate will not dissolve.

20.2.9 Cool the solution to room temperature, make to 250 mL, and mix thoroughly.

20.2.10 A ten-fold dilution of this solution in 2 % nitric acid is necessary for ICP-AES or AAS analysis for metals.

20.2.11 See Appendix X2 for examples of analytical data using solutions from these fusions.

## 21. Precision and Bias

21.1 This practice addresses only the preparation steps in the overall preparation and measurement of the sample analytes. Since the preparation alone does not produce any results, the user must determine the precision and bias resulting from this preparation and subsequent analysis.

## PRACTICE 3—DISSOLUTION OF GLASS USING A MICROWAVE OVEN

### 22. Scope

22.1 This practice describes a microwave oven practice used to dissolve glass samples that may contain nuclear wastes. The resulting solutions are then used to determine metals and radionuclides in support of glass vitrification plant operations and materials development programs. This practice can be used to dissolve production glass samples, vitrified melter feeds, and sludges.

### 23. Summary of Practice

23.1 The glass samples are ground to a fine powder and digested in a microwave oven using a mixture of hydrofluoric and nitric acids. The sample is then further digested after the

addition of hydrochloric acid and boric acid. Boron is added to the resulting solution to complex fluoride ions and to aid in the dissolution of low-solubility metal fluorides. The solution can then be analyzed for metals and radionuclides.

23.2 Boron may interfere with determining certain elements of interest, so the user may process two sample aliquots with one containing no added boron.

## 24. Significance and Use

24.1 This practice details microwave oven methods to dissolve vitrified feed and product glasses for determining concentrations of metals and radionuclides. Microwave oven dissolution of glass samples as described in this practice is used to dissolve samples for subsequent analysis for metals and radionuclides.

24.2 This dissolution method is suitable for dissolving samples of canistered glass containing nuclear wastes with analyte recoveries that are suitable for process control, waste acceptance, and durability testing as described in Refs (3) and (4).

24.3 The practice will dissolve vitrified melter feed with recovery of analytes satisfactory for glass plant process control.

24.4 This microwave dissolution practice, when used in conjunction with standard practices for alkaline flux fusion of glass (Practices C 1342 and C 1317), can provide solution suitable for determining most metals, radionuclides, and anions of interest.

24.5 The solutions resulting from this practice (after necessary dilutions and preparations) are suitable for analysis by ICP-AES as described in Test Methods C 1109 and C 1111, ICP-MS, AAS, ion chromatography, and radiochemical methods.

24.6 This practice can be used to dissolve glass samples for bulk characterizations in support of the PCT as described in Test Methods C 1285.

## 25. Interferences

25.1 Boron cannot be determined in the solutions obtained from this practice since it is added to complex excess fluoride ions. Boron may be determined using the fusion dissolutions described in Section 11 or 20 of this practice.

25.2 Silicon cannot be determined unless an acid-resistant sample introduction system is used on the ICP-AES or ICP/MS spectrometers. Since Si is the matrix, quantitation is normally not required. However, Si may be measured by fusing the glass using the alkaline fusion dissolution practices described in Section 11 or 20.

25.3 Some elements such as Th and the rare earths may not dissolve. An alkaline fusion of the glass using Section 11 or 20 of this practice may be necessary for quantitative recoveries of these elements.

25.4 Elements that form volatile fluorides may be lost if the microwave digestion vessels vent prior to cooling.

25.5 Low recoveries of Cr, Ni, and Zn may occur due to the addition of boric acid. These elements should be determined in a sample aliquot prior to the addition of the boric acid.

25.6 Incomplete dissolution of some samples may result

using the parameters of this practice if the sample is not ground less than 100 mesh.

NOTE 6—The user should determine the recoveries of all elements of analytical interest through comparison of experimental results to values of known materials.

## 26. Apparatus

26.1 *Laboratory Microwave Oven*, with pressure and temperature control and a digestion vessel capping station.

NOTE 7—A remotely operated microwave oven and capping station may be necessary if shielded operations are required to prevent exposure to sample radiation. Conditions for remote operations may be determined on the bench top/hood and then used to estimate oven parameters for shielded operations without the need for pressure and temperature sensors. Use of microwave sensors in a hot cell may be prohibitive.

26.2 *PTFE Microwave Digestion Vessels*, with rupture membranes and capable of containing pressures greater than 120 % of the expected operating pressure. Digestion vessel venting and pressure monitoring capability is needed.

26.3 *Analytical Balance*, capable of weighing to  $\pm 0.1$  mg.

26.4 *Polypropylene, Polyethylene or PTFE Bottles and Volumetric Flasks*, of sufficient quantity and size to meet sample and reagent storage and handling needs.

## 27. Reagents

27.1 *Purity of Reagents*—Reagent grade chemicals must be used for all dissolutions and method blanks. Unless specified, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.<sup>5</sup> Other grades may be used, if it is ascertained that the reagent is of sufficiently high purity to permit its use without reducing the accuracy of the determination.

27.2 *Hydrofluoric Acid* (48 to 51 % w/w), concentrated hydrofluoric acid (29 M HF).

27.3 *Nitric Acid* (sp gr 1.42), concentrated nitric acid (16 M HNO<sub>3</sub>).

27.4 *Hydrochloric Acid* (sp gr 1.18), concentrated hydrochloric acid (12 M HCl).

27.5 *Boric Acid*, reagent grade.

27.6 *Boric Acid Solution*, 0.6 M, dissolve 37.5 g of boric acid into 1 L of water in a polypropylene bottle.

## 28. Hazards

28.1 Many of the vitreous feeds and the product glasses from vitrification plants will be radioactive requiring the user of this practice to adhere to site radiation protection practices to avoid exposure to radiation. The microwave dissolution may need to be performed in shielded hoods, glove boxes or hot cells.

28.2 Hydrofluoric acid can cause severe burns upon skin contact that will require special medical attention. Inhalation of HF vapors will cause severe lung damage.

28.3 Microwave digestion vessels operate at high temperature and pressure. The operator must follow all safety precautions for cooling and handling as outlined in the manufacturer's instructions and in-site specific safety guidance.

## 29. Sample Preparation

29.1 Glass and vitrifier feed samples should be ground to



100 mesh or to a “powdery” consistency prior to weighing into the microwave dissolution vessel. Grinding can be done using an agate mortar and pestle if this introduces no contaminants of interest.

29.2 A tungsten carbide grinding apparatus may also be used and will minimize addition of contaminants of interest to the sample.

### 30. Procedure

30.1 Tare an aluminum weighing boat or a microwave digestion vessel on the analytical balance.

30.2 Weigh  $0.25 \pm 0.01$  g of the ground sample into the boat or digestion vessel.

NOTE 8—The amount of sample taken can vary depending upon the waste loading of the glass, the analytical sensitivity needed, and the radiation levels encountered. The user of this practice should determine the optimum sample size through experimentation with actual materials.

30.3 Transfer the sample quantitatively to the microwave digestion vessel if a weighing boat was used for the initial sample aliquoting.

30.4 Pipette 5 mL of reagent water into the weighing boat, swirl gently, and then pour into the microwave digestion vessel. Various acids may be used to transfer the contents of the boat to the vessel, but the user must establish potential interference effects.

30.5 Pipette 5 mL of nitric acid and 5 mL of hydrofluoric acid to the microwave digestion vessel and swirl the vessel gently to mix the contents.

30.6 Cap the vessels using the capping station, swirl each vessel to ensure uniform mixing, and then place the vessels symmetrically in the round vessel holder. The use of a capping station is optional.

30.7 Follow laboratory and manufacturer’s operating directions for loading the vessels and connecting the temperature and pressure indicators and for shielded facility operations.

30.8 Microwave the samples at 100 psi for 15 min.

30.9 Cool the vessels in an ice bath for at least 30 min to ensure ambient pressure. Vent the vessels following established laboratory operating practice.

NOTE 9—The microwave vessels and contents must be cool to ambient temperature prior to uncapping or the cap will blow off violently expelling the contents.

30.10 Add 5 mL of concentrated hydrochloric acid and 40 mL of the 0.6 M boric acid solution to each vessel.

30.11 Reserve an aliquot for analysis without the addition of boric acid for determination of metals subject to low recoveries in the presence of boron.

30.12 Recap the vessels, place them in the holder, reconnect vent tubes and monitoring sensors (if used).

30.13 Redigest the samples at 80 psi for an additional 30 min.

30.14 After cooling, uncap the vessels and transfer the contents of the vessels to a 200 mL PTFE volumetric flask and make to volume with water.

NOTE 10—If internal standards or yield tracers are desired, add these prior to making the sample solution to volume.

30.15 A method blank should be prepared by adding all reagents to a digestion vessel and carrying the solution through the entire process. Also prepare a duplicate and matrix spike sample for QA parameter determination.

### 31. Precision and Bias

31.1 This practice addresses only the preparation steps in the overall preparation and measurement of analytes in nuclear waste containing glass and thus does not produce any measurements. Hence a statement of precision and bias is not meaningful.

31.2 Data obtained from round-robin glass samples using this dissolution method and subsequent analysis by ICP-AES, AAS, and radiochemical methods are reported in Refs (5) and (6).

### 32. Keywords

32.1 alkaline fusion; borosilicate glass; dissolving glass; ICP-AES; ICP-MS; microwave digestion; nuclear waste in glass

APPENDIXES

(Nonmandatory Information)

X1. EXAMPLE ANALYSES OF GLASS USING THE Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-Na<sub>2</sub>CO<sub>3</sub> FUSION PRACTICE

X1.1 This procedure addresses only the preparation steps in the overall preparation and measurement of the sample analytes. Since the preparation alone does not produce any results, the user must determine the precision and bias resulting from this preparation and subsequent analysis.

X1.2 The data given in Tables X1.1-X1.3 provide an indication of expected precision and bias when using this dissolution procedure to analyze standard reference glasses. These data were obtained by analyzing aliquots of the dissolved sample using ICP-AES. Tables X1.1-X1.3 show the known target composition, mean weight percent found using this dissolution, and standard deviation and percent relative standard deviation (RSD)

TABLE X1.1 Fusion Dissolution, ARG Glass

N = 36 <sup>A</sup>				
Oxide	Target <sup>B</sup> Wt %	Mean Wt %	Standard Deviation	% RSD
Al <sub>2</sub> O <sub>3</sub>	4.53	4.73	0.022	0.5
Cr <sub>2</sub> O <sub>3</sub>	0.096	0.093	0.001	0.8
SiO <sub>2</sub>	48.6	47.9	0.157	0.3
TiO <sub>2</sub>	1.12	1.15	0.007	0.6

<sup>A</sup>Six samples of the same glass were ground independently. Each sample was dissolved in triplicate, and each dissolution was analyzed on the ICP in duplicate.

<sup>B</sup>Target composition.

TABLE X1.3 Fusion Dissolution, NIST SRM 93a

N = 2 <sup>A</sup>				
Oxide	Target <sup>B</sup> Wt %	Mean Wt %	Standard Deviation	% RSD
Al <sub>2</sub> O <sub>3</sub>	2.2 (8)	2.29	0.021	0.9
SiO <sub>2</sub>	80.8	80.4	0.071	0.1

<sup>A</sup>The sample was ground, dissolved in duplicate, and analyzed by ICP.

<sup>B</sup>National Institute for Standards and Technology supplied data. The numbers in parentheses are for information only and are not considered significant.

TABLE X1.2 Fusion Dissolution, WVRG-6 Glass

N = 6 <sup>A</sup>				
Oxide	Target <sup>B</sup> Wt %	Mean Wt %	Standard Deviation	% RSD
Al <sub>2</sub> O <sub>3</sub>	6.00	6.02	0.052	0.9
BaO	0.16	0.14	0.004	3.0
CaO	0.48	0.57	0.013	2.3
CoO	0.02	0.019	0.001	3.0
Cr <sub>2</sub> O <sub>3</sub>	0.14	0.17	0.005	3.3
CuO	0.03	0.055	0.002	3.9
Fe <sub>2</sub> O <sub>3</sub>	12.02	11.9	0.207	1.8
MgO	0.89	0.92	0.021	2.2
MnO <sub>2</sub>	1.01	1.09	0.021	1.9
SiO <sub>2</sub>	40.98	40.9	0.283	0.7
SrO	0.02	0.024	0.000	0.0
TiO <sub>2</sub>	0.80	0.80	0.019	2.4
ZnO	0.02	0.031	0.001	2.0
ZrO <sub>2</sub>	1.32	1.30	0.035	2.7

<sup>A</sup>Three samples of the same glass were ground independently. Each sample was dissolved in duplicate and analyzed on the ICP.

<sup>B</sup>Target composition.

X2. EXAMPLE ANALYSES OF GLASS USING THE KOH AND Na<sub>2</sub>O<sub>2</sub> FUSION PRACTICES

X2.1 Tables X2.1-X2.4 are included to demonstrate analytical recoveries experienced by a single laboratory using this fusion dissolution practice followed by ICP-AES analysis of the dissolved samples. The reference glasses used are: Table X2.1—EA reference glass values were established by the manufacturer; Table X2.2—Analytical Reference Glass-1 (ARG-1) reference values were established by the manufacturer; Tables X2.3 and X2.4—reference values are from National Institutes of Standards and Technology (NIST) certificates for the glass SRMs used. The EA and ARG-1 glasses were special production and not generally available.

X2.4, both the KOH and Na<sub>2</sub>O<sub>2</sub> fusions were used to dissolve each of the standard glasses. With the following exceptions, the results in the tables are an average from both fusions:

Na<sub>2</sub>O concentrations are from the KOH fusion only,  
NiO concentrations are from the Na<sub>2</sub>O<sub>2</sub> fusion only, and  
ZrO<sub>2</sub> concentrations are from the KOH fusion only.

X2.3 Analytical results for K<sub>2</sub>O are not presented since ICP-AES does not have a sufficient lower quantitation limit for this element. Potassium can be determined from a Na<sub>2</sub>O<sub>2</sub> fusion of the glass sample followed by atomic absorption spectroscopy analyses.

X2.2 To determine the suite of elements on Tables X2.1-



**TABLE X2.1 Results from Analysis of EA Reference Glass**

	Weight % Oxide		Difference	Percent Difference
	Determined Value	Reference Value		
Al <sub>2</sub> O <sub>3</sub>	3.71	3.70	0.01	0.27
B <sub>2</sub> O <sub>3</sub>	11.0	11.28	-0.28	-2.48
CaO	1.17	1.12	0.05	4.46
Fe <sub>2</sub> O <sub>3</sub>	9.48	7.38	2.10	28.46
La <sub>2</sub> O <sub>3</sub>	0.42	0.42	0.00	0.00
K <sub>2</sub> O	<sup>A</sup>	0.04	...	...
Li <sub>2</sub> O	4.27	4.26	0.01	0.23
MgO	1.73	1.72	0.01	0.58
MnO	1.35	1.34	0.01	0.75
Na <sub>2</sub> O	14.3	16.8	-2.50	-14.88
NiO	0.59	0.57	0.02	3.51
SiO <sub>2</sub>	49.6	48.7	0.90	1.85
TiO <sub>2</sub>	0.70	0.70	0.00	0.00
ZrO <sub>2</sub>	0.47	0.46	0.01	2.17

<sup>A</sup>Potassium is not reported on ICP data.

**TABLE X2.2 Results from Analysis of Analytical Reference Glass-1**

	Weight % Oxide		Difference	Percent Difference
	Determined Value	Reference Value		
Al <sub>2</sub> O <sub>3</sub>	4.69	4.73	-0.04	-0.85
B <sub>2</sub> O <sub>3</sub>	8.35	8.67	-0.32	-3.69
BaO	0.087	0.088	-0.001	-1.14
CaO	1.50	1.53	-0.03	-1.96
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.093	0.007	7.53
CuO	not detected	0.004	...	...
Fe <sub>2</sub> O <sub>3</sub>	14.6	14	0.6	4.29
K <sub>2</sub> O	<sup>A</sup>	2.71	...	...
Li <sub>2</sub> O	3.20	3.21	-0.01	-0.31
MgO	0.86	0.86	0	0.00
MnO <sub>2</sub>	2.27	2.31	-0.04	-1.73
Na <sub>2</sub> O	11.2	11.5	-0.3	-2.61
NiO	1.06	1.05	0.01	0.95
P <sub>2</sub> O <sub>5</sub>	0.36	0.25	0.11	44.00
SiO <sub>2</sub>	49.1	47.9	1.2	2.51
SrO	0.005	0.0037	0.0013	35.14
TiO <sub>2</sub>	1.15	1.15	0	0.00
ZnO	0.02	0.02	0	0.00
ZrO <sub>2</sub>	0.14	0.13	0.01	7.69

<sup>A</sup>Potassium is not reported on ICP data.

**TABLE X2.3 Results from Analysis of SRM 1411 Borosilicate Glass**

	Weight % Oxide		Difference	Percent Difference
	Determined Value	SRM 1411 Value		
Al <sub>2</sub> O <sub>3</sub>	5.61	5.68	-0.07	-1.17
B <sub>2</sub> O <sub>3</sub>	10.57	10.94	-0.37	-3.41
BaO	4.82	5.00	-0.18	-3.60
CaO	2.13	2.18	-0.05	-2.14
Fe <sub>2</sub> O <sub>3</sub>	0.11	0.05	0.06	120.00
K <sub>2</sub> O	<sup>A</sup>	2.97	...	...
MgO	0.36	0.33	0.03	8.08
Na <sub>2</sub> O	9.85	10.14	-0.29	-2.86
SiO <sub>2</sub>	55.49	58.01	-2.52	-4.35
ZnO	3.95	3.85	0.10	2.60

<sup>A</sup>Potassium is not reported on ICP data.


**TABLE X2.4 Results from Analysis of SRM 1412 Borosilicate Glass**

	Weight % Oxide		Difference	Percent Difference
	Determined Value	SRM 1412 Value		
Al <sub>2</sub> O <sub>3</sub>	7.42	7.52	-0.10	-1.33
B <sub>2</sub> O <sub>3</sub>	4.39	4.53	-0.14	-3.09
BaO	4.44	4.67	-0.23	-4.93
CaO	4.55	4.53	0.02	0.44
CdO	4.31	4.38	-0.08	-1.71
Fe <sub>2</sub> O <sub>3</sub>	0.06	0.031	0.02	77.42
K <sub>2</sub> O	<sup>A</sup>	4.14	...	...
Li <sub>2</sub> O	4.34	4.5	-0.17	-3.67
MgO	4.45	4.69	-0.25	-5.61
Na <sub>2</sub> O	4.82	4.69	0.13	2.77
PbO	4.46	4.4	0.06	1.36
SiO <sub>2</sub>	40.25	42.38	-2.14	-5.04
ZnO	4.45	4.48	-0.04	-0.78

<sup>A</sup>Potassium is not reported on ICP data.

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