

Standard Test Method for Determining Liquidus Temperature of Immobilized Waste Glasses and Simulated Waste Glasses¹

This standard is issued under the fixed designation C1720; 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.

 ϵ^1 NOTE—Units statement was editorially corrected in April 2015.

1. Scope

1.1 These practices cover procedures for determining the liquidus temperature $(T_{\rm L})$ of nuclear waste, mixed nuclear waste, simulated nuclear waste, or hazardous waste glass in the temperature range from 600°C to 1600°C. This method differs from Practice C829 in that it employs additional methods to determine $T_{\rm L}$. $T_{\rm L}$ is useful in waste glass plant operation, glass formulation, and melter design to determine the minimum temperature that must be maintained in a waste glass melt to make sure that crystallization does not occur or is below a particular constraint, for example, 1 volume % crystallinity or $T_{1\%}$. As of now, many institutions studying waste and simulated waste vitrification are not in agreement regarding this constraint (1).

1.2 Three methods are included, differing in (1) the type of equipment available to the analyst (that is, type of furnace and characterization equipment), (2) the quantity of glass available to the analyst, (3) the precision and accuracy desired for the measurement, and (4) candidate glass properties. The glass properties, for example, glass volatility and estimated $T_{\rm I}$, will dictate the required method for making the most precise measurement. The three different approaches to measuring $T_{\rm L}$ described here include the following: (A) Gradient Temperature Furnace Method (GT), (B) Uniform Temperature Furnace Method (UT), and (C) Crystal Fraction Extrapolation Method (CF). This procedure is intended to provide specific work processes, but may be supplemented by test instructions as deemed appropriate by the project manager or principle investigator. The methods defined here are not applicable to glasses that form multiple immiscible liquid phases. Immiscibility may be detected in the initial examination of glass during sample preparation (see 9.3). However, immiscibility may not become apparent until after testing is underway.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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
- C162 Terminology of Glass and Glass Products
- C829 Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E2282 Guide for Defining the Test Result of a Test Method 2.2 *Other Documents:*
- 2.2 Other Documents:
- SRM-773 National Institute for Standards and Technology (NIST) Liquidus Temperature Standard
- SRM-674b NIST X-Ray Powder Diffraction Intensity Set for Quantitative Analysis by X-Ray Diffraction (XRD)
- SRM-1976a NIST Instrument Response Standard for X-Ray Powder Diffraction
- Z540.3 American National Standards Institute/National Conference of Standards Laboratories (ANSI/NCSL) Requirements for the Calibration of Measuring and Test Equipment

3. Terminology

3.1 Definitions:

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.13 on Spent Fuel and High Level Waste.

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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.

3.1.1 *air quenching*—to pour or place a molten glass specimen on a surface, for example, a steel plate, and cool it to the solid state.

3.1.2 *anneal*—to prevent or remove materials processing stresses in glass by controlled cooling from a suitable temperature, for example, the glass transition temperature (T_g) (modified from Terminology C162).

3.1.3 *annealing*—a controlled cooling process for glass designed to reduce thermal residual stress to an acceptable level and, in some cases, modify structure (modified from Terminology C162).

3.1.4 ASTM Type I water—purified water with a maximum total matter content including soluble silica of 0.1 g/m³, a maximum electrical conductivity of 0.056 $\mu\Omega$ /cm at 25°C and a minimum electrical resistivity of 18 M Ω × cm at 25°C (see Specification D1193 and Terminology D1129).

3.1.5 *cleaning glass*—glass or flux used to remove high viscosity glass, melt insolubles, or other contamination from platinum-ware.

3.1.6 *crystallize*—to form or grow, or both, crystals from a glass melt during heat-treatment or cooling.

3.1.7 *crystallization*—the progression in which crystals are first nucleated and then grown within a host medium. Generally, the host may be a gas, liquid, or another crystalline form. However, in this context, it is assumed that the medium is a glass melt.

3.1.8 *crystallization front*—the boundary between the crystalline and crystal-free regions in a test specimen that was subjected to a temperature gradient heat-treatment.

3.1.9 *furnace profiling*—the process of determining the actual temperature inside of a furnace at a given location; this involves different processes for different types of furnaces.

3.1.10 *glass*—an inorganic product of fusion that has cooled to a rigid condition without crystallizing (see Terminology C162); a noncrystalline solid or an amorphous solid (2).³

3.1.11 *glass ceramic*—solid material, partly crystalline and partly glassy (see Terminology C162).

3.1.12 *glass sample*—the material to be heat-treated or tested by other means.

3.1.13 *glass specimen*—the material resulting from a specific heat treatment.

3.1.14 glass transition temperature (T_g) —on heating, the temperature at which a glass transforms from a solid to a liquid material, characterized by the onset of a rapid change in several properties, such as thermal expansivity.

3.1.15 *gradient furnace*—a furnace in which a known temperature gradient is maintained between the two ends.

3.1.16 *hazardous waste glass*—a glass composed of glass forming additives and hazardous waste.

3.1.17 *homogeneous glass*—a glass that is a single amorphous phase; a glass that is not separated into multiple amorphous phases.

3.1.18 *inhomogeneous glass*—a glass that is not a single amorphous phase; a glass that is either phase separated into multiple amorphous phases or is crystallized.

3.1.19 *liquidus temperature*—the maximum temperature at which equilibrium exists between the molten glass and its primary crystalline phase.

3.1.20 *melt insoluble*—a crystalline, amorphous, or mixed phase material that is not appreciably soluble in molten glass, for example, noble metals, noble metal oxides.

3.1.21 *mixed waste*—waste containing both radioactive and hazardous components regulated by the Atomic Energy Act (AEA) (3) and the Resource Conservation and Recovery Act (RCRA) (4), respectively; the term "radioactive component" refers to the actual radionuclides dispersed or suspended in the waste substance (5).

3.1.22 *mold*—a pattern, hollow form, or matrix for giving a certain shape or form to something in a plastic or molten state. Webster's⁴

3.1.23 *nuclear waste glass*—a glass composed of glass-forming additives and radioactive waste.

3.1.24 *observation*—the process of obtaining information regarding the presence or absence of an attribute of a test specimen or of making a reading on a characteristic or dimension of a test specimen (see Terminology E2282).

3.1.25 *phase separated glass*—a glass containing more than one amorphous phase.

3.1.26 *preferred orientation*—when there is a stronger tendency for the crystallites in a powder or a texture to be oriented more one way, or one set of ways, than all others. This is typically due to the crystal structure. $IUCr^5$

3.1.27 *primary phase*—the crystalline phase at equilibrium with a glass melt at its liquidus temperature.

3.1.28 *radioactive*—of or exhibiting radioactivity; a material giving or capable of giving off radiant energy in the form of particles or rays, for example, α , β , and γ , by the disintegration of atomic nuclei; said of certain elements, such as radium, thorium, and uranium and their products. American Heritage⁶ Webster's⁷

3.1.29 *Round-Robin*—an interlaboratory and intralaboratory testing process to develop the precision and bias of a procedure.

3.1.30 *section*—a part separated or removed by cutting; a slice, for example, representative thin section of the glass specimen. Webster's⁴

3.1.31 *set of samples*—samples tested simultaneously in the same oven.

³ The boldface numbers in parentheses refer to a list of references at the end of this standard.

⁴ Webster's New Universal Unabridged Dictionary, 1979.

⁵ IUCr Online Dictionary of Crystallography, 2011.

⁶ American Heritage Dictionary, 1973.

⁷ Webster's New Twentieth Century Dictionary, 1973.

3.1.32 *simulated nuclear waste glass*—a glass composed of glass forming additives with simulants of, or actual chemical species, or both, in radioactive wastes or in mixed nuclear wastes, or both.

3.1.33 *standard*—to have the quality of a model, gage, pattern, or type. Webster's⁷

3.1.34 *standardize*—to make, cause, adjust, or adapt to fit a standard (5); to cause to conform to a given standard, for example, to make standard or uniform. Webster's⁷

3.1.35 *surface tension*—a property, due to molecular forces, by which the surface film of all liquids tends to bring the contained volume into a form having the least possible area.

3.1.36 *test determination*—the value of a characteristic or dimension of a single test specimen derived from one or more observed values (see Terminology E2282).

3.1.37 *test method*—a definitive procedure that produces a test result (see Terminology E2282).

3.1.38 test observation—see observation.

3.1.39 *test result*—the value of a characteristic obtained by carrying out a specific test method (see Terminology E2282).

3.1.40 *uniform temperature furnace*—a furnace in which the temperature is invariant over some defined volume and within some defined variance.

3.1.41 *vitrification*—the process of fusing waste with glass making chemicals at elevated temperatures to form a waste glass (see Terminology C162).

3.1.42 *volatility*—the act of one or more constituents of a solid or liquid mixture to pass into the vapor state.

3.1.43 *waste glass*—a glass developed or used for immobilizing radioactive, mixed, or hazardous wastes.

3.2 Abbreviations:

3.2.1 AEA—Atomic Energy Act

3.2.2 ANSI-American National Standards Institute

3.2.3 ASTM-American Society for Testing and Materials

3.2.4 CF—crystal fraction extrapolation

3.2.5 C_F —crystal fraction in a sample or specimen

3.2.6 EDS-energy dispersive spectrometry

3.2.7 η—viscosity

3.2.8 FWHM-full width of a peak at half maximum

3.2.9 GF-gradient temperature furnace

3.2.10 GT-gradient temperature

3.2.11 HF-hydrofluoric acid

3.2.12 *HLW*—high-level waste

3.2.13 ID-identification

3.2.14 *NBS*—National Bureau of Standards

3.2.15 NCSL—National Conference of Standards Laboratories

3.2.16 *NIST*—National Institute for Standards and Technology (formerly NBS)

3.2.17 OM—optical microscope or optical microscopy

3.2.18 *PDF*—powder diffraction file

3.2.19 RCRA-Resource Conservation and Recovery Act

3.2.20 RIR—relative intensity ratio

3.2.21 RLM-reflected light microscopy

3.2.22 SEM—scanning electron microscope or scanning electron microscopy

3.2.23 SRM—Standard Reference Material

3.2.24 $T_{1\%}$ —temperature where glass contains 1 volume % of a crystalline phase

3.2.25 T_a —primary UT measurement above T_L

3.2.26 T_c —primary UT measurement below T_L

3.2.27 T_g —glass transition temperature

3.2.28 T_L —liquidus temperature

3.2.29 TLM-transmitted light microscopy

3.2.30 T_{M} —melting temperature for glass preparations

3.2.31 UF—uniform temperature furnace

3.2.32 *UT*—uniform temperature

3.2.33 WC-tungsten carbide

3.2.34 XRD-X-ray diffraction

4. Summary of Test Method

4.1 This procedure describes methods for determining the $T_{\rm L}$ of waste or simulated waste glasses. Temperature is defined as the maximum temperature at which equilibrium exists between the molten glass and its primary crystalline phase. In other words, $T_{\rm L}$ is the maximum temperature at which a glass melt crystallizes. Fig. 1 illustrates an example $T_{\rm L}$ for a simple two-component liquid on a binary phase diagram.

4.1.1 (A) Gradient Temperature Furnace Method (GT)— This method is similar to Practice C829, "Standard Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method," though it has been modified to meet the specific needs of waste and simulated waste glass measurements. The most pronounced differences between this method and the Practice C829 "boat method" are the sample preparation and examination procedures.

4.1.1.1 Samples are loaded into a boat, for example, platinum alloy (Fig. 2) with a tight-fitting lid, and exposed to a linear temperature gradient in a gradient furnace (Fig. 3) for a fixed period of time. The temperature, as a function of distance, d, along the sample, is determined by its location within the GF, and the $T_{\rm L}$ is then related to the location of the crystallization front in the heat-treated specimen (Fig. 4).

4.1.1.2 Following the heat-treatment, the specimen should be annealed at or near the glass transition, $T_{\rm g}$, of the glass (this should be previously measured or estimated) to reduce specimen cracking during cutting and polishing.

4.1.1.3 The specimen should then be scored or marked to signify the locations on the specimen located at different depths into the gradient furnace, that is, locations heat-treated at specific temperatures.

4.1.1.4 If the specimen is optically transparent, it can be observed with transmitted light (that is, transmitted light microscopy or TLM) or reflected light microscopy (RLM) to look for bulk or surface crystallization, respectively. If the specimen is not optically transparent or is barely optically



FIG. 2 GF Boat Diagram: (A) Single Chamber Crucible Design (B) Single Chamber Design Loaded with a Set of Samples (that is, Smaller Crucibles)

transparent (for example, in high iron glasses with high quantities of FeO), a cut or fractured section of the glass can be polished very thin (that is, a thin section can be made) to allow for observation. Another option for surface observations is scanning electron microscopy (SEM). This method provides a quick measurement of $T_{\rm L}$ in the absence of convective flow of glass in the GF, which distorts the crystallization front (that is, the crystallization front shall not be constant with melt height).

4.1.1.5 The temperature gradient and increased volatility at higher temperatures cause gradients in surface tension, which in turn cause convective flow. This method is ideal for glasses

with a $T_{\rm L}$ less than roughly 1000°C or glasses with a low volatility near the $T_{\rm L}$. If the temperature range spanned by the crystallization front is too high for the desired tolerance, the UT or CF methods (Method B or C) should be used for a more precise $T_{\rm L}$ measurement. Method A is not easily used to measure the $T_{\rm L}$ on radioactive glasses because of the size of the GF and the complicated sample analysis required. This method is not recommended for glasses with a $T_{\rm L}$ in a temperature range of very low glass viscosity (that is, $\eta < 50$ Pa × s).

4.1.2 (B) Uniform Temperature Furnace Method (UT)— This method is similar to the methods used in phase diagram

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FIG. 3 Photograph of Typical Gradient Temperature Furnace



FIG. 4 OM Micrograph of the Crystallization Front in a GT Specimen

determination and can be used for more precise measurements than those determined with (A) Gradient Temperature Furnace Method (GT).

4.1.2.1 In this method, a glass sample is loaded into a crucible (for example, platinum alloy, see Fig. 5) with a tight-fitting lid and subjected to temperatures for a fixed period of time (for example, 24 ± 2 hrs). Following heat-treatment, the specimen can be observed by optical microscopy (OM) for the appearance or absence of crystalline or other undissolved materials with methods similar to those previously described (4.1.1).

4.1.2.2 The $T_{\rm L}$ is then given by the temperature range between the highest temperature at which a specimen contains crystals ($T_{\rm c}$) and the lowest temperature without crystals in the specimen ($T_{\rm a}$); the $T_{\rm L}$ is then typically defined as the average of $T_{\rm a}$ and $T_{\rm c}$.

4.1.2.3 This method is more time consuming as it requires multiple heat-treatments than the GT method, though it minimizes the effects of volatility and eliminates the convectiondriven uncertainty in crystallization front measurements. This method is used for high precision measurements (on the order of $\pm 5^{\circ}$ C), is more easily applied to radioactive glasses, and is capable of measuring $T_{\rm L}$ values as high as 1600°C with typical high-temperature furnaces (for example, furnaces with MoSi₂ heating elements) though higher with specialized equipment and high-temperature crucibles. This method may be used for glasses with a high volatility near $T_{\rm L}$ under certain circumstances.

4.1.3 (C) Crystal Fraction Extrapolation Method (CF)— This method is an alternate method that uses a UT specimen to measure the crystal fraction, $C_{\rm F}$ (in mass % or volume %), of a crystalline phase or phases in a sample heat-treated at multiple temperatures, $T << T_{\rm L}$. The $C_{\rm F}$ at each temperature is measured with XRD, RLM, TLM, or SEM, or combinations thereof, by mass % or by volume %, or both, and then $T_{\rm L}$ is achieved by extrapolating $C_{\rm F}$ as a function of temperature to zero crystals. This method is more suited for glasses with a higher volatility near the $T_{\rm L}$ than the previous methods. When multiple crystalline phases are present, XRD is an effective method for quantifying $C_{\rm F}$ as a function of temperature and is



(1) 3.6- \times 3.6-cm square piece of foil (A) or conical thimble (B) made of inert material, for example, platinum alloy



(2) For the cubic crucible, take foil in (1) and draw an " \times " pattern from corner to corner (excluding the center square) to help locate the form used and where to fold the corners.



(3) Fold the corners along the diagonal lines. Then fold the sides up next to the form. FIG. 5 UF Crucible Schematic

very effective at determining the $T_{\rm L}$ of each phase indepen-

dently; this would be more difficult with Methods A or B. The

 $C_{\rm F}$ method yields the additional benefit of equilibrium crystal fractions as a function of temperature, which can sometimes tend to be non-linear at $C_{\rm F} > 5$ to 10 mass % crystallinity for most crystalline phases. Different techniques for the $C_{\rm F}$ method are described below.

4.1.3.1 Volume Fraction of Crystal(s) in the Specimen (12.4.2)—With TLM, RLM, or SEM as well as image analysis software (to define area fractions of glass and crystal phases), it is possible to measure the area fraction of crystals in an image or micrograph of the specimen, typically a micrograph. The area fraction is then equivalent to the volume fraction if the image is representative of the specimen, and the effective depth of the image is insignificant. If this process is done at different temperatures, the $T_{\rm L}$ can be extrapolated as a function of temperature.

Note 1—The mass fraction of crystals in the specimen can be estimated if the density of the glass and the crystal(s) is known.

4.1.3.2 Number Fraction of Crystal(s) in the Specimen (12.4.3)—In the same fashion as described in 4.1.3.1, count the number of crystals in an image or micrograph of the specimen at different temperatures. If this process is done at different temperatures, the $T_{\rm L}$ can be extrapolated as a function of temperature.

4.1.3.3 Mass Fraction of Crystal(s) in the Specimen by Adding a Known Crystalline Phase (12.4.4)—Adding a known mass fraction of a known, standard crystalline material (for example, NIST SRM-674b) allows the standardization of the XRD pattern. The standards and the unknown specimen should be run in independently before mixing to verify that there is not overlap between the peaks of the standard and the peaks in the unknown specimen because this will make quantification difficult and less accurate. The standardized pattern can then be used to generate quantitative (if the crystal structure has been refined) or semi-quantitative (if the crystal structure has not been refined) C_F analysis with Rietveld (6-8) refinement software or the relative intensity ratio (RIR) method (12.4.5).

4.1.3.4 Mass Fraction of Crystal(s) in the Specimen by Comparing it to the Calibration Curve (12.4.5)—In this method, samples with known concentrations of the crystalline phases being analyzed are prepared and tested using XRD. The peak area's (full width at half maximum or FWHM, total crystal peak area, or highest peak area) and known crystal fractions are used to generate a calibration curve. The peak area of the unknown specimen is then used in the calibration equation to determine a quantitative (if interpolated) or semiquantitative (if extrapolated) crystal fraction.

4.1.3.5 Volume Fraction of Crystal(s) in the Specimen With C_F Data From XRD Analysis—Commonly, melter constraints are in terms of a volume % of crystallinity, for example, 1 volume % or $T_{1\%}$. Once C_F data are obtained in mass % by XRD, the remaining mass of glass, m_g , is calculated as a difference given by

$$m_{g} = m_{t} - \sum_{i=1}^{N} m_{c,i}$$
(1)

 m_t = the total mass (that is, the value is normalized to one and thus component values are mass fractions), and

where:

 $m_{c,i}$ = the mass fraction of the *i*-th crystalline phase observed and quantified by XRD.

By converting the mass fractions of the *i*-th component additives, m_i , into mole fractions, M_i , the density of glass, ρ_g , can be computed with the following expression:

$$\rho_g = \frac{\sum_{i=1}^{N} M_i m_{m,i}}{\sum_{i=1}^{N} M_i V_{M,i}}$$
(2)

where:

 $m_{m,i}$ = the molecular mass of the *i*-th oxide, and $V_{M,i}$ = the molar volume of the *i*-th component additive explained elsewhere (9).

The total volume of each heat treatment, $V_{\rm HT}$, is calculated with

$$V_{HT} = \frac{m_g}{\rho_g} + \frac{\sum_{i=1}^{N} m_{c,i}}{\rho_{c,i}}$$
(3)

where:

 $\rho_{c,i}$ = the density of the *i*-th crystalline component.

The volume % of the *i* -th crystalline component, $V_{c,i}$, in the heat-treated specimen is denoted by

$$V_{c,i} = 100 \times \frac{m_{c,i}}{\left(\rho_{c,i} \times V_{HT}\right)} \tag{4}$$

The values of $V_{c,i}$ can then be plotted as a function of temperature and a linear correlation fit to the data with

$$V_{c,i} = m \times T + b \tag{5}$$

where:

 $T_{1\%} = (V_{c,i} - b)/m$ when $V_{c,i} = 1 (T_{1\%})$

5. Significance and Use

5.1 This procedure can be used for (but is limited to) the following applications:

(1) support glass formulation development to make sure that processing criteria are met,

(2) support production (for example, processing or troubleshooting), and

(3) support model validation.

6. Apparatus

6.1 Equipment for the GT Method:

6.1.1 Resistance-heated tubular gradient furnace capable of achieving temperatures of 550 to 1150°C with gradients in the range of roughly 1°C/mm (Fig. 3). For glasses with an estimated $T_{\rm L} > 1150$ °C, furnaces with elements capable of high temperatures need be used, for example, MoSi₂.

6.1.2 Calibrated thermocouple and temperature readout device appropriate to the estimated temperature range that will be used for testing. Type K can be used within 95 to 1260°C, Type R can be used within 870 to 1450°C, and Type S can be used within 980 to 1450°C without special calibrations or qualifications.

6.1.3 Resistance furnace and controller used for annealing (capable of maintaining constant temperatures between 400 and ~ 900°C) with a temperature accuracy of 10° C.

6.1.4 Specimen boat made of material inert to the sample (for example, platinum alloy) with approximate dimensions of $0.5 \times 1 \times 10$ to 30 cm (width × height × length), respectively; an example specimen boat is shown in Fig. 2. If the test glass viscosity is below 5 Pa × s at the measurement temperature, it is recommended that a round-based crucible be used. A separate option with Method A is to fill the long boat with several small individual boats with individual lids (Fig. 2-B)

6.1.5 Diamond cutoff saw.

6.1.6 Variable speed polisher.

6.1.7 Silicone rubber mold for mounting of GT glass specimen in epoxy.

6.1.8 OM for TLM and RLM.

6.1.9 Scanning electron microscope with energy dispersive spectrometer.

6.1.10 X-ray diffractometer.

6.2 Equipment Needed for the UT Method:

6.2.1 Resistance furnace capable of maintaining constant temperatures $T \sim 550$ to 1600° C (that is, MoSi₂ heating elements) or furnace capable of $T \leq 1200^{\circ}$ C for glasses with $T_{\rm L} \leq 1150^{\circ}$ C.

6.2.2 Calibrated thermocouple and temperature readout device appropriate to the estimated temperature range that will be used for testing (6.1.2).

6.2.3 Specimen boat (or crucible) and tight fitting lid made of material compatible with the sample (for example, platinum alloy) with suggested dimensions of $1.2 \times 1.2 \times 1.2$ cm (width \times height \times length, respectively) (Fig. 5-1A). Another option is a round-bottom, thimble-shaped crucible (Fig. 5-1B).

6.2.4 Diamond cutoff saw.

6.2.5 Variable speed polisher.

6.2.6 OM with variable power transmitted and reflected light.

6.2.7 SEM/energy dispersive spectrometry (EDS).

6.2.8 XRD.

6.3 Equipment needed for the CF method includes the same equipment as described previously in 6.2 because a UT specimen is required for the measurement technique, though additional materials are also required.

6.3.1 Image analysis software for measuring the $C_{\rm F}$ present in a micrograph collected with OM, SEM, etc.

6.3.2 Crystal structure/unit cell refinement software for quantifying crystal fractions by spiking in a known mass% of a known crystalline material.

6.3.3 Known crystalline material (for example, SRM-674b) that does not overlap with crystalline peaks in unknown specimen.

7. Reagents and Materials

7.1 Reagents and materials used in conjunction with the various methods outlined in this procedure.

7.1.1 Reagents:

7.1.1.1 ASTM Type 1 water.

7.1.1.2 Cleaning solvents, for example, ethanol, isopropanol, acetone.

7.1.1.3 Abrasive media for polishing, for example, SiC, diamond.

7.1.1.4 Glass microscope slides.

7.1.1.5 Glass cover slides.

7.1.1.6 Temperature sensitive adhesive.

7.1.1.7 Solvent-soluble adhesives, for example, methyl methacrylate-based adhesives.

7.1.1.8 Non-temperature sensitive adhesives (such as cyanoacrylate or other epoxy).

7.1.2 Materials:

7.1.2.1 Furnace appropriate to method being used, for example, GF, UF (required heating elements dependent on temperature needs).

7.1.2.2 Material for making crucibles or boats, for example, sheets of platinum alloy or pre-formed crucible(s).

7.1.3 *Calibrated Thermocouples*—Type K can be used within 95 to 1260°C, Type R can be used within 870 to 1450°C, and Type S can be used within 980 to 1450°C without special calibrations or qualifications.

7.1.3.1 Standard reference material for calibrating furnace, for example, SRM-773.

7.1.3.2 OM or SEM for making visual observations of heat-treated specimens.

7.1.3.3 XRD for making $C_{\rm F}$ measurements.

7.1.3.4 XRD standard reference material for peak location and $C_{\rm F}$ calibration (for example, SRM-1976a).

8. Hazards

8.1 The hazards associated with this procedure should be evaluated by each institution before conducting work.

8.2 The primary hazards encountered when following this procedure are sharp objects (for example, metal foil for crucibles, glass shards, and saws), high-temperature surfaces (for example, furnace surfaces, heat-treated specimens fresh out of a furnace, tongs used to remove specimens from a furnace), electrical hazards (for example, exposed heating elements such as MoSi₂), and radiation hazards (for example, if working with radioactive waste, when using XRD). When handling a glass specimen, protective gloves should be worn to prevent injury. The furnaces used for heat-treatment of the glass samples outlined in this procedure are at temperatures of 600 to 1600°C, and therefore temperature-resistant or insulated gloves should be worn when putting samples into the furnace as well as removing specimens from the furnace. Electrically insulating gloves should also be used in conjunction with (that is, underneath) the leather gloves to electrically isolate the user's hands from potential contact of the tongs or tweezers with exposed electrical elements used in removing heat-treated specimens. It is pertinent that the operator of the XRD is cautious of the hazards associated with the technique and is trained to the institution's safety procedures for operating the equipment.

9. Sampling, Test Specimens, and Test Units

9.1 Specific test instructions will contain all or part of the following information: preferred $T_{\rm L}$ measurement method, tolerance goals, estimated $T_{\rm g}$ (needed for Method A only), an estimated $T_{\rm L}$ or temperature range (based on model predictions), heat treatment time, and data recording requirements.

9.2 GF Preparation:

9.2.1 A gradient furnace is constructed of two or more independent heating zones, and thus the gradient can be adjusted as needed to obtain a low-pitched $(\Delta T/\Delta d \text{ is low}, where T \text{ is temperature and } d \text{ is distance from a reference point inside the furnace) or sharp gradient } (\Delta T/\Delta d \text{ is high}) that is dependent on the crystallization rate of the sample } (\Delta C_F/\Delta T). If <math>\Delta C_F/\Delta T$ is low (for example, $\Delta C_F/\Delta T \leq 1 \text{ mass } \% \Delta C_F$ increase over $\geq 100^{\circ}\text{C}$ is considered low), the gradient can be low-pitched, and in cases where $\Delta C_F/\Delta T$ is high ($\Delta C_F/\Delta T \geq 1 \text{ mass } \% \Delta C_F$ increase over $\leq 10^{\circ}\text{C}$ is considered extremely high), the gradient can be high-pitched.

9.3 Sample Preparation for Methods A, B, and C:

9.3.1 Glass samples for $T_{\rm L}$ analysis are typically melted, ground to a powder and mixed, remelted, and then quenched on a steel plate. Once quenched, analyze the glass sample with OM, SEM, or XRD, or combinations thereof, to make sure that the sample is free of crystalline and immiscible glass phases. Melt insolubles (for example, noble metal oxides) are acceptable, but should be reported. If the sample is crystal free and homogeneous, then follow 9.3.2 – 9.3.4. However, if the glass is crystallized or otherwise inhomogeneous, then skip to step 9.3.5.

9.3.2 According to Practice C829, the particle sizes recommended for $T_{\rm L}$ determination of the SRM-773 glass with Method A (boat method) is < 0.85 mm (-20 mesh) and with Method B (perforated plate) is between 1.70 and 2.36 mm (+12/-8 mesh). However, in practice, glass particles that are too small (that is, ≤0.100 mm) when heat-treated can introduce a significant degree of bubbles into the melt, especially in moderate and high viscosity glasses ($\eta > 10 \text{ Pa} \times s$), which can dramatically affect heat transfer as well as visibility through a heat-treated glass specimen. Also, it is difficult to clean glass particles that are too small (that is, ≤ 0.100 mm). Glass particles that are too large (that is, >4 mm) will not fit in the previously described crucibles. Thus, the recommended particle size for these measurements is between 0.422 mm and 4 mm or (+40/-5 mesh); thus the glass should be sieved and this size retained. These sizes are used because sizes << 0.422 mm will promote crystal nucleation and growth during heat treatments, and sizes >> 4.0 mm pose a issues when attempting to load glass into the crucible because the packing density is reduced significantly. Carefully crush the glass, being cautious not to introduce contamination (that is, no direct contact with steel). Use a mill or mortar and pestle composed of material harder than the glass (for example, SiC, WC, or equivalent) to crush the sample to the desired size.

9.3.3 Wash the sample by ultrasonic cleaning for 2 min in a clean glass beaker or equivalent container by submerging glass particles in ASTM Type 1 water, which fills the container above the glass by an equivalent volume. Decant the water and repeat the ultrasonic cleaning twice more (2 min each cleaning) with fresh ASTM Type 1 water. Ultrasonically clean the sample a fourth time for 2 min with ethanol. Decant the ethanol and dry the sample at \geq 90°C for \geq 1 hr in an open beaker in an oven designed for drying combustibles. The washing steps can be performed using alternative, non-polar solvents (for example, pentane, hexane) if a reaction between water or the solvent and the glass is suspected.

9.3.4 Transfer the cleaned and dried glass sample into a clean, marked container or bag, being careful not to contaminate the glass with dust, dirt, oils, or salts or cross-contaminate the sample with other samples. Seal the container or bag and store in a clean, dry environment until ready for testing.

9.3.5 Glasses that are crystallized, inhomogeneous, or phase separated should be prepared by grinding the entire batch to a very fine powder. The grinding and mixing will best homogenize the glass. It is essential to reduce the effects of sample inhomogeneity when making $T_{\rm L}$ measurements.

10. Preparation of Apparatus

10.1 *Furnace Setup*—The furnace should be capable of sustaining temperatures that will be used for heat treatments with \geq 50°C between the furnace's maximum operating temperature and the heat-treatment temperature. The furnace should have a calibrated temperature monitoring capability. The furnace should have an over-temperature control to prevent damage to the furnace by potential heating past the maximum operating temperature of the furnace. See 6.1 and 6.2 for further information.

10.2 Specimen Preparation for Analysis—See 12.2.4 for instructions on preparing specimens for the GT method, 12.3.2 for instructions on preparing specimens for the UT method, and the 12.4 subsections for instructions on preparing specimens for the different CF methods.

10.3 Analysis Equipment:

10.3.1 *OM*—OM can be used to observe heat-treated specimens in TLM or RLM mode (depending on specimen optical transparency and morphology). For image analysis in Method C, the microscope should be equipped with a micrograph acquisition system (for example, digital camera).

10.3.2 *SEM*—Specimen preparation for general SEM observations typically requires that the specimen be coated with an electrically conductive coating (for example, C, Au, Pd) unless the SEM can analyze low-conductivity specimens. For high-resolution SEM micrograph acquisition, specimens can either be polished (best if done to optical quality) to expose the features of interest on a surface of the specimen, or they can remain unpolished.

10.3.3 *XRD*—Typical specimen preparation for XRD involves grinding a heat-treated specimen to a powder. To verify peak locations, the powdered specimen should be doped with an approved XRD standard, for example SRM-1976a.

11. Calibration and Standardization

11.1 *Calibration*—The test equipment, including thermocouples and thermocouple readouts, must be calibrated, at least annually, in accordance with a consensus standard, for example, ANSI/NCSL Z540.3.

11.1.1 Furnaces must be profiled for temperature at least once every six months and checked for accuracy at least once every six months during active projects. Profiling of the GF shall be performed according to Practice C829 (see 11.1.1.1).

11.1.1.1 The GF can be profiled by inserting a calibrated thermocouple into the furnace, while empty, and measuring the equilibrium temperature at different distances, d, from a location (typically a stopper inserted at the back end). Use the

gradient furnace temperature profile to determine the length of the specimen boat and the position where the boat is placed in the gradient furnace. If the gradient is non-linear, the different heating zones can be adjusted accordingly until the desired gradient and gradient shape are achieved. The temperature gradient in the GF should be close to linear ($\pm 1^{\circ}$ C over the temperature range of interest) with a gradient of no more than 1.2°C/mm. Then, the gradient furnace should be operated with standard reference materials for temperature calibration, for example, SRM-773.

11.1.1.2 To profile a UF, create a sample stage inside of the furnace in the middle of the hot zone of the furnace. Then, make sure that there are an adequate number of holes through the top of the furnace that are large enough to fit the width of a thermocouple (~ 0.6 cm) directly above the positions labeled on the sample stage. Holes not in use should be plugged to prevent heat loss and unwanted temperature gradients. If using Example (B) in Table, then nine holes must be made in the top of the furnace directly above the locations being profiled.

11.1.1.3 The furnace is to be profiled through a temperature range of a given test. For instance, if the furnace is going to be used to test samples in the range of 810 to 1290°C, then the furnace should be profiled at 800°C, 1300°C, and a regular temperature increment in between (for example, every 100°C from 800 to 1300°C). Note that not all thermocouples can be calibrated through this entire range, so make sure that a calibration curve is used for each type of thermocouple to extrapolate the actual temperature value from the voltage reading on the thermocouple readout if the thermocouple being used is outside of the range (for example, Type R/S at $T \ge 1450^{\circ}$ C).

11.1.1.4 At each temperature, place the calibrated thermocouple through the hole in the top of the furnace and rest the end of the thermocouple at the location where the sample crucible shall be located on the sample stage. Note that electrical safety procedures must be followed when working near electrical hazards. Let the temperature come to thermal equilibrium (for example, 5 to 20 min) at each location and record the reading from the thermocouple in the profiling table (see example in Table). If a temperature value at a given location on the sample stage at a given temperature is $\pm 5^{\circ}$ C different from the average temperature over the other profiling locations, then data collected at that location at that temperature should not be used for the T_c/T_a values used to determine T_L . Therefore, samples for T_c and T_a values used to determine T_L should be run at a location on the sample stage that is different from any locations that are out of tolerance.

11.1.2 The XRD should be calibrated every six months or at the completion of any maintenance. To do this, perform an XRD scan on a 2θ calibration standard (for example, SRM-1976a) and verify that the diffraction peak locations (that is, degrees, 2θ) and intensities match those of the standard. If peaks are not in the correct locations, then the instrument must be realigned.

11.2 *Measurement Control*—At least one standard glass with $T_{\rm L}$ traceable to a round robin study or NIST standard (that is, SRM-773) shall be tested with each new batch of $T_{\rm L}$ measurements or on a regular frequency to determine the accuracy of each furnace over time. The minimum frequency shall be measured once annually or with each change of furnace profile or gradient, whichever comes first. The measured value must be within the tolerance expected for the standard glass, or the furnace must be re-configured and the standard re-measured. The data from these tests should be maintained, plotted, and analyzed to check for trends, biases, or increases in variation as part of a defined measurement control program. This can provide continuous validation of the test method and basis for bias adjustments.

12. Procedure

12.1 Liquidus temperature measurements of a glass specimen shall be determined by one of three methods: (A) Gradient Temperature Furnace Method (GT), (B) Uniform Temperature Furnace Method (UT), or (C) Crystal Fraction Extrapolation Method (CF). The appropriate method for the samples to be tested shall be specified in the applicable test instructions. For GT specimens, proceed to 12.2; for UT specimens, proceed to 12.3; for CF specimens, proceed to 12.4.

12.2 Gradient Temperature Furnace Method (GT):

TABLE 1 Furnace Profiling Diagram



NOTE 1—(A) Shows a circular sample stage example and (B) shows a square sample stage example. The tabulated data to the right of the diagrams shows how the thermocouple readouts are entered at each temperature for each position. Locations at temperatures that are more than $\pm 2^{\circ}$ C from the average temperatures collected at a specific temperature are to be omitted from use for T_a or T_c values—these values are to be labeled as red, bold, or underlined, or combinations thereof.

12.2.1 Place test glass sample in a boat (6.1) and slide into a preheated and profiled gradient furnace (11.1.1.1) through the cooler end of the furnace. Position the boat in the furnace at the desired test temperature range. Let the glass sample soak for the time specified in the test instruction. The typical heat treatment time is 24 ± 2 hr, though this is determined by the time required to reach thermal equilibrium.

12.2.2 At the completion of the heat treatment, remove the boat with the specimen from the gradient furnace and place into a preheated annealing furnace with the temperature near the measured or estimated T_g for ≥ 2 hr and then slowly cool the furnace to room temperature.

12.2.3 Remove the boat from the annealing furnace and mark the specimen in a way to correlate locations on the specimen with d and T values (4.1.1). Remove the test specimen from the boat, attempting to keep the specimen intact. Depending on the crystallization rate of the glass tested, the low-temperature end of the heat-treated specimen might appear to be a heavily crystallized glass ceramic. Place the specimen in a mold, for example, silicone rubber, large enough to fit the entire specimen or, at the very least, the region of intended interest (estimated $T_L \pm 5$ cm). Cover the specimen entirely with a single batch of epoxy. Allow the epoxy to cure and harden. Remove the specimen from the mold. This process will improve the ability to keep the specimen intact during cutting and polishing.

12.2.4 Use a saw equipped with a diamond cut-off blade to cut the specimen in half longitudinally, along the temperature gradient, and polish the cut side of one of the halves. Adhere the polished side to a single or to multiple glass microscope slides (for example, with cyanoacrylate or CrystalBond); it is typically easier to polish multiple small sections (\leq 5 cm, each)

versus one large section due to the reduced friction on the polisher. Cut the remainder of the specimen parallel to the slide, leaving ~ 2 to 4 mm thick of specimen adhered to the slide, and polish a thin section of the specimen with a variable speed polisher. Polish the opposite side of the specimen. Make sure to permanently mark the identification of the specimen, the gradient profile, and the profile measurement increments on the glass slide. Fig. 6 shows an example of a properly prepared specimen.

12.2.5 After the specimen thin-section has been prepared, analyze the specimen with OM or SEM, or both, to determine the location of the crystallization front (Fig. 4). In the absence of convection, the $T_{\rm L}$ of a glass is equal to or higher than the temperature of the crystallization front. The crystallization front may span a range of several degrees as shown in Fig. 7. In this case, record the range of temperatures in which the crystallization front occurs. If the temperature range of the crystallization front several degrees goals, the sample must be retested with a smaller gradient or with Methods B or C.

12.2.6 The $T_{\rm L}$ should be taken as the temperature in the center of the crystallization front temperature range (see Fig. 4) unless other evidence suggests that a different temperature within the range should be selected.

12.2.7 Determine the crystalline phase with OM or SEM, or both. Additional analysis can be done to provide more definitive information such as EDS or XRD, or both, if requested by the test originator.

12.2.8 Record date, sample name, gradient profile, primary phase, analysis technique, crystallization front temperature range, and liquidus temperature measurement for each glass in a Laboratory Record Book or data sheet.



NOTE 1—In sequence from the top are (1) platinum boats filled with small platinum crucibles with lids, (2) an entire gradient furnace heat-treated specimen mounted in epoxy and labeled accordingly, (3) epoxy mounted specimens longitudinally cut into smaller sections, and (4) thin sections of gradient furnace specimens.

FIG. 6 Prepared GT Specimen for Analysis



FIG. 7 Crystallization Front in GT Specimen with Convective Flow Patterns

12.3 (B) Uniform Temperature Furnace Method (UT):

12.3.1 Place the test glass sample in a box or conical crucible (6.2) and place it into a preheated and profiled uniform temperature furnace. Position the crucible in the furnace at the proper location as per the furnace profiling from 11.1.1.2. Let the glass sample soak for the specified time. It is recommended that tests be run \geq 24 hr for $T \geq$ 900°C, \geq 48 hr for $T \sim$ 800°C, \geq 72 hr for $T \sim$ 700°C, \geq 84 hr for $T \sim$ 650°C to reach thermal equilibrium, even though these times are sample dependent and subject to change on a per-glass basis.

12.3.1.1 The thermal equilibrium can be determined for a given sample at a specific temperature by running several identical samples in parallel and removing them from the furnace at different time points to monitor the $C_{\rm F}$ as a function of time. The time at which $C_{\rm F}$ plateaus is considered equilibrium. If the samples are held at too high of a temperature (sample dependent), materials in the glass could volatilize off and change the composition of the glass, thus artificially changing the properties and altering the measurement of true thermal equilibrium.

12.3.2 At the completion of the heat treatment, air-quench the specimen and remove the test glass specimen from the crucible. Water quenching can be used for samples that are predicted to phase separate or crystallize rapidly upon cooling. For quenching in liquids, however, the liquid should only contact the outside surfaces of the crucible to prevent chemical reaction with the glass inside the crucible. Prepare the specimen sections with the example in Fig. 8 as a guide. If the glass is shattered, as is common with water quenching, simply adhere the broken fragments to the slide.

12.3.2.1 Make the "Initial Cut" on the specimen diagonally with a diamond-impregnated blade as seen in Fig. 8-B, and then Part (1) is labeled and put aside. It is ideal to use a thinner blade (200 to 300 μ m) versus a thicker blade (>300 μ m) to

minimize the stresses introduced to the specimen by the blade as well as the amount of glass lost due to the cutting.

12.3.2.2 Polish the surface of the remaining specimen, that is, the boundary between (1) and (2), and adhere to a microscope slide, for example with cyanoacrylate or equivalent.

12.3.2.3 Add a single cover slip to each side of the slide as seen in Fig. 8-C-(b). These cover slips provide a high-surfacearea stopping point in the polishing procedure so the specimen is not polished away completely and also assist in keeping the polishing plane parallel to the plane of the slide. For most specimens, a thickness comparable to that of the cover slip (that is, 250 μ m) is sufficiently thin to observe the specimen with TLM at magnifications ~ 250×; however, some specimens will need to be polished thinner for TLM observations.

12.3.2.4 The specimen should be cut at the "Final Cut" region in Fig. 8-B, between (2) and (3), and then polished to a final thickness close to that of the cover slip, yielding a "Thin Section" of the specimen as seen as the geometry in Fig. 8-D (as well as Fig. 8-C-(c)). Unannealed glass may form glass shards during slide preparation.

(1) Due to the abrasive nature of the diamond saw blades, sometimes a rough grit (that is, >100 μ m or 120 grit) might be required to planarize the specimen, that is, place the entire exposed surface on a single polished plane. However, typically ~ 50- μ m (240-grit) sandpaper is a good starting point for polishing glass.

(2) Once the specimen is polished down, that is, planar with the cover slips, higher grit number papers are used (smaller diamond or SiC grain sizes). A good procedure to use from here is 25 μ m (400 grit), 16 μ m (600 grit), 12 μ m (800 grit), and 6 μ m (1200 grit). Cloth pads with diamond suspensions and diamond-impregnated cloth pads can be used to substitute for sandpaper because sandpaper does not last as long as the others, though it is less expensive to replace.



FIG. 8 Schematic of How the Isothermal Heat Treatment Specimen Should Be Cut for Thin Section Observation With Transmitted-Light OM

(A) shows the oblique view of the appearance of a glass specimen following a heat treatment inside of a crucible as seen in Fig. 5.

(3) If high magnification OM or SEM is required, ≤ 3 -µm particle size diamond suspensions can be used in conjunction with cloth pads for higher quality polishing.

12.3.2.5 Permanently mark the identification of the test specimen (for example, on the back of the slide where it will not be polished away accidentally), the temperature used, the furnace used, the date of the heat treatment, and the duration of the heat treatment on the glass slide. A good practice is to cover the label with tape to prevent it from getting polished or wiped away during the specimen preparation process.

12.3.3 Analyze the thin-section with TLM (bulk measurement), RLM or SEM (surface measurement), or combinations thereof, to determine if the specimen contains crystals. The $T_{\rm L}$ of the glass shall lie between $T_{\rm c}$ and $T_{\rm a}$.

12.3.4 Repeat steps 12.3 - 12.3.3 while altering the heattreatment temperature accordingly until the temperature range is narrowed to a sufficient degree of tolerance (for example, 10° C) as dictated by the data need. The $T_{\rm L}$ is typically the average of $T_{\rm c}$ and $T_{\rm a}$; however, careful OM examinations by an experienced researcher may allow more precise $T_{\rm L}$ estimation.

12.3.5 Determine the crystalline phase with OM and SEM for morphology, EDS for composition, XRD, or combinations thereof, for structure and general composition.

12.3.6 Record sample name, date of heat treatment, final actual temperature, duration of test, presence of crystalline phases, and analysis technique for each specimen as well as T_L for each different glass being tested in a study in a laboratory record book, data sheet, or other as per test instruction. The actual temperature is determined by the difference between the thermocouple readout and the T_L determined for the internal standard glass. This difference needs to be applied to all temperatures recorded during testing. See Appendix X1 for an example of how heat treatment data can be logged for determining T_L for a test instruction.

12.4 (C) Crystal Fraction Extrapolation Methods (CF):

12.4.1 The first step to this procedure is to run a GT heat treatment with several individual boats in the long trough boat or a series of UT heat treatments at different temperatures. If GT specimens are being used, a temperature range of each boat must be noted (translated as a temperature error bar for $C_{\rm F}$ measurements).

12.4.2 Volume Fraction of Crystal(s) in the Specimen—this can be done with RLM, SEM, or XRD methods, or combinations thereof, though XRD methods are described separately (12.4.4 – 12.4.5). For RLM and SEM, similar sampling regions should be compared in specimens at different temperatures (for example, look at the center of the bottom region of all specimens); see Fig. 9-A.

12.4.2.1 Polish the specimen to a high-quality finish; for example, a diamond suspension of size $\leq 3 \mu m$ is recommended as a suitable final polishing medium.

12.4.2.2 Capture a minimum of 3 (preferably ≥ 10 for good statistics) micrographs of the specimen surface with appropriate brightness and contrast so the crystals can be distinguished from the glass matrix.

12.4.2.3 Analyze the micrographs with image analysis software to determine the area in the field of view that has crystals as compared to that which does not contain crystals. This ratio is equivalent to the volume fraction of a crystal(s) in the specimen if the depth of the field is insignificant. Report the average volume fraction of the samplings taken along with the standard error.

12.4.3 Number Fraction of a Crystal(s) in the Specimen— This method is similar to 12.4.2, though the number of crystals in an image or micrograph of a specimen is measured (instead of the volume of crystals) and heat-treated at a specific temperature. Repeat this process on specimens of the sample heat-treated at different temperatures and plot the crystal



FIG. 9 (A) Crystalline Area (%) as a Function of Temperature with T_L Extrapolated at 1040°C, (B) Number of Crystals Measured at Different Temperatures with T_L Extrapolated at 1033°C. These measurements were collected on Round-Robin Glass A (15.1.5) (10).

number as a function of temperature. The $T_{\rm L}$ is equivalent to the temperature at which the crystal number is zero; see Fig. 9-B.

12.4.4 Mass Fraction of Crystal(s) in the Specimen by Doping with Known Crystalline Phase—This method requires an XRD.

12.4.4.1 Collect the portion of the specimen labeled (1) in Fig. 8-B. The preferred sample mass for XRD analysis is typically ≥ 1 g, though this is dependent on the XRD method being employed and the volume required to fill the XRD sample holder.

NOTE 2—It is good practice to use a sample holder of the same size for a series of measurements on a single sample to help reduce error associated with XRD analysis.

12.4.4.2 Grind the specimen from 12.4.4.1 in a mill or mortar and pestle. Weigh the powdered specimen on a calibrated balance with sufficient precision (for example, ± 0.1 mg) and add a known amount (for example, 5 mass %) of an internal standard powder (for example, SRM-674b) to the powdered specimen and re-grind. Be sure that the diffraction peaks associated with the specimen do not overlap with those of the standard to prevent adding errors associated with the peak quantifications, for example, analyze the specimen before doping with the standard. Do not over-grind in this step, or you can turn some of the standard amorphous, skewing the quantification. The suggested grinding time for glass specimens is 2 min (based on preparation of typical HLW glasses). Different glasses may require more or less time than the suggested 2 min. In some cases, grinding times of over 2 min with a WC milling chamber have introduced significant amounts of WC into the sample and were identified in the XRD scan. These peaks can interfere with phase identification (ID) and whole-pattern fitting. Also, it will contaminate the XRD specimen. Record the mass of the specimen and the internal standard and then calculate the actual mass % of the internal standard with the following expression:

where:

 m_s = the mass of the standard added, and

 m_m = the mass of the specimen material (glass with included phases).

mass $\% = \frac{m_s}{(m_m + m_s)} \times 100$

This information is to be used during data analysis after obtaining the XRD pattern. Avoid preparing specimens several times larger than needed. This may add unnecessary inhomogeneity problems.

12.4.4.3 After grinding, the specimen is a fine powder and should be transferred from the mill or mortar to a sample vial inside a fume hood to minimize breathing harmful dust particles.

12.4.4.4 Mount the spiked powder specimen to an XRD sample holder and try to achieve random packing to avoid preferred orientation which can make data interpretation difficult. It is recommended that a rotating sample holder be used to minimize the effects of preferred orientation on the results of this quantitative procedure. The manner in which the sample is mounted can have a significant impact on the results, depend-

ing on the structure of the phases present in the specimen. Sample mounting must be consistent to minimize mounting errors.

12.4.4.5 Perform XRD analysis on spiked specimen. Typical values include a step range of 0.04° 20 and a scan range of 5 to 75° 20, though parameters will vary, depending on the type of XRD, the sensitivity of the X-ray detector, and the crystal-line phase(s) present in the specimen.

12.4.4.6 Identify the primary and secondary crystalline phases by analyzing the diffraction patterns. The primary phase is the majority phase.

12.4.4.7 Once the phases have been identified, use cell refinement software to quantify the $C_{\rm F}$ of phases present in mass % (this can prove difficult if the exact crystal composition is unknown). Graph the $C_{\rm F}$ as a function of temperature (°C) of the heat treatment as a function of the mass % of the primary phase identified as seen in Fig. 10-A and fit a linear trendline to the data. Solve for x when y = 0 ($C_{\rm F} = 0$) to get the $T_{\rm L}$. Another method is to invert the axes and use the y-intercept as the $T_{\rm L}$ (Fig. 10-B). This process requires ≥ 2 data points, but preferably more, to make sure that the trend in the data is a real trend.

12.4.5 Mass Fraction of Crystal(s) in the Specimen by Comparing to Calibration Curve—This method requires an XRD. In this method, specimens are compared to a calibration curve for a specific crystalline phase(s), which is created beforehand, and the mass % is extrapolated from the calibration curve for each crystalline phase present in the specimen.

12.4.5.1 The first step of creating the calibration curve for a specific glass study is to find a representative, crystal-free, base glass for the study; this is typically referred to as a baseline glass.

12.4.5.2 Then, it is necessary to determine which crystalline phases might be found in the course of the $T_{\rm L}$ study (for example, spinel, nepheline) and find pure sources of these phases in powder or bulk form.

12.4.5.3 To create a calibration curve for each individual crystalline phase, several different specimens need to be made with different known mass percentages of each phase doped into the baseline glass encompassing the range of crystallinity that is expected for the given study (that is, if the study shall produce glasses with no more than 10 mass % of that particular phase, then the calibration curve only needs to be extended to ~ 10 mass %—a very high value).

12.4.5.4 Each sample made for the calibration curve must be powdered and doped with an internal standard (for example, SRM-674b) at a known mass fraction. The strength of the X-ray tube on the XRD diminishes with time, and therefore an internal standard must be run for each sample for the sample to be comparable to samples run previously or on other XRD instruments. The manner in which the sample is mounted can have a significant impact on the results. Sample mounting must be consistent to minimize mounting errors. For this reason, it is recommended that each operator measure and create a separate calibration curve.

12.4.5.5 Analyze the specimens with XRD. In XRD pattern analysis software, analyze the 100 % intensity peak (primary peak) for that crystalline phase and measure the peak area.

(6)



FIG. 10 (A) Regular Fit of Mass% Spinel as a Function of Temperature for US-13 Glass (11). (B) Inverse Fit of Real Data of Temperature as a Function of Mass % Spinel.
NOTE: This can be done for all phases identified by XRD in a specimen, and in this particular example, spinel was the primary phase identified.

Graph the area of the 100 % intensity peak as a function of mass fraction of the crystalline phase (Fig. 11). Fit a linear

trendline to the data to establish a correlation between the mass % of the phase and the area of the 100 % peak.



FIG. 11 Area of 100 % Peak of Magnetite (Fe₃O₄) and Fluorite (CaF₂) Versus Spiked Mass % of Magnetite With XRD. For Each of these Tests, 5 Mass % Peak of Fluorite was Added to the Specimen as an Internal Standard.

12.4.5.6 Once this calibration curve is established for a given base glass and a given crystalline phase, the calibration curve can be used to determine the mass fraction of a crystalline phase in an unknown specimen that was not run through the doping mass fraction procedure outlined in 12.4.5.3 – 12.4.5.5. Take a UT specimen, dope it with a known mass % of a known crystalline phase (for example, SRM-674b) as seen in 12.4.4.2, grind up the specimen with the dopant (9.3 and 12.4.4.3), and analyze with XRD following steps outlined in 12.4.4.4 – 12.4.4.7. The unknown should also be doped with an XRD standard (that is, SRM-674b) and analyzed by XRD for comparison purposes (that is, XRD tube strength over time).

12.4.5.7 Once XRD has been run on the doped specimen and the primary phases identified and quantified, the data for each phase identified can be then compared to the established calibration curve for that particular phase in 12.4.5.3. Then the actual mass % can be calculated from the function fit to the calibration data.

12.4.5.8 Once peak area data are collected, the RIR can be determined with the following expression:

$$RIR = \frac{A_u I_s g_s}{A_s I_u g_u} \tag{7}$$

where:

g = mass fraction,

A = peak area,

I = peak intensity, that is, peak intensity/intensity of 100 % peak, and

u and *s* = the unknown and standard crystal, respectively (subscripts).

Plot RIR versus inverse g_u to determine whether the RIR remains constant over the range of g_u measured. If there are significant deviations from a constant g_u , then RIR should be fit by the appropriate function that can be used to interpolate to the RIR used to evaluate unknown mass fractions.

12.4.6 *RIR Method*—Quantification or semi-quantification of mass fraction(s) of crystalline phase(s) in a glass by comparing the RIR of different crystalline phase(s) to that of a reference standard (for example, Al_2O_3).

12.4.6.1 Once the crystalline phases are identified, determine the peak areas.

(1) Measure the area of the tallest peak of a given phase that is not affected by another phase in the specimen, avoiding measuring peaks that significantly overlap with another crystalline phase in the specimen. Calculating areas that overlap can have significant error associated with them.

(2) If using a manually fit background, make sure that the background fit is accurately simulated. If the background is not correct, then change the background fitting parameters to achieve the most accurate fit.

12.4.6.2 For quantitative results, a calibration curve must be measured and used to calculate the RIR of the phase(s) identified within the host (for example, simulated waste glass) matrix (12.4.5). For semi-quantitative analyses, obtain an RIR from the powder diffraction file (PDF) card and proceed to the following step. If it is not possible to determine an RIR, and

one is not available in the PDF card, then this method should not be used to determine the concentration of that phase.

12.4.6.3 The following expression can be used to solve for the mass fraction of the phase(s) in the specimen with unknown concentrations:

$$g_u = \frac{A_u}{A_s} \frac{I_s}{I_u} \frac{g_s}{RIR}$$
(8)

If the RIR is unknown, proceed to 12.4.5 to measure it for a given phase.

13. Calculation or Interpretation of Results

13.1 *GT Method*—refer to sections 12.2.5 – 12.2.7.

13.2 UT Method—refer to sections 12.3.3 – 12.3.5.

13.3 CF Method—refer to section 12.4.

14. Report

14.1 Report all results and test determinations from the analysis of a glass or batch of glasses. Temperatures are to be reported in degrees Celsius (°C). The report shall typically include the information described below.

14.1.1 Glass identification.

14.1.2 Requestor.

14.1.3 Test instruction number.

14.1.4 Request date.

14.1.5 Crystallization front temperature range (Method A) or T_a and T_c (Methods B and C).

14.1.6 $T_{\rm L}$ or range if uncertain.

14.1.7 $C_{\rm F}$ as a function of temperature (Method C).

14.1.8 Analysis technique(s) used, for example, OM, SEM, EDS, and XRD.

14.1.9 Analysis data, for example, micrographs, XRD traces, and EDS spectra.

14.1.10 Primary and secondary crystalline phase(s).

14.1.11 Any deviations or discrepancies.

14.1.12 Furnace profile and date.

14.1.13 Standard glass values and date.

14.1.14 Laboratory record book, electronic database, or data sheet references.

14.1.15 Temperature reading device, that is, thermometers, type of thermocouples, etc.

14.1.16 Equipment calibration information.

15. Precision and Bias

15.1 Precision-Test Methods A, B, and C.

15.1.1 The data used to generate the measures of precision for $T_{\rm L}$ testing are the result of intra- and interlaboratory Round-Robin testing. These measures are typical of the methods as applied to the glasses and standards used in the Round-Robin, and are not all inclusive with respect to other types of glasses. The measures of precision were determined in accordance with procedures in Practices E177 and E691. These measures are designated as follows:

15.1.2 *Repeatability*—the standard deviation for withlaboratory determinations.

15.1.3 *Reproducibility*—the standard deviation for betweenlaboratory determinations. 15.1.4 % *RSD*—the standard deviation divided by the consensus mean and multiplied by 100 %.

15.1.5 T_L Methods GT, UT, and CF: Intra- and Interlaboratory Precision Determination—A Round-Robin was completed between 10 laboratories to determine the repeatability of these methods. Three glasses were distributed to these facilities. Not all laboratories were able to take part in all three techniques for all glasses. The three glasses, A (10), B (12), and C (13-15), tested in this Round-Robin had T_L values of ~ 961 \pm 9.26°C (zircon, ZrSiO₄), 1040 \pm 11.54°C (spinel, NiFe₂O₄), and 1226 \pm 7.221°C (rare-earth borosilicate, Nd₃BSi₂O₁₀), respectively, as averaged over all data points for all methods; see Table 2. Micrographs captured of the crystalline phases in the Round-Robin glasses are presented in Fig. 12. These values suggest that the precision of a T_L measurement on a given glass should be within \pm 10°C of the actual value across all methods.

15.1.6 *GT Method*—Insufficient data were gathered to determine the precision of this method as only a few of the laboratories had this capability. Through participation between two laboratories, a $T_{\rm L,R}$ of 32°C was demonstrated with this method for Glass A. More data points are necessary for this method to determine a true precision with a standard deviation. However, Practice C829 states that the precision of two independent tests in the same furnace is generally within 10°C.

15.1.7 *UT Method*—Through participation between eight laboratories, the UT method proved to be the most precise method with a variability of 6.9 to 7.5°C, depending on the glass tested.

15.1.8 *CF Method*—This method showed the largest $T_{L,R}$ (37°C) for the data set (Glass A). T_L measurements collected with the CF methods were comparable to those collected with the UT method.

15.2 Bias:

15.2.1 For $T_{\rm L}$ Methods A, B, and C, the average $T_{\rm L}$ values for the standard glasses tested here allow the assessment of long term bias or variability of the $T_{\rm L}$ test, for example, how reproducible the experiment variables such as oven temperature, sieving, heat-treatment analysis, are over time. The use of a standard glass (also including SRM-773). allows inter-laboratory long-term and short-term variables to be bias corrected. Use of the standard glass also allows data from different laboratories to be compared on an equivalent basis by bias correction of the intra-laboratory variables.

16. Keywords

16.1 calibration; gradient furnace; liquidus temperature; uniform temperature furnace

TABLE 2 Summary Results for T_L Round Robin Study

Note $1-T_{L,min}$ is the minimum measured value for a particular glass and method, $T_{L,max}$ is the maximum measured value for a particular glass and method, and $T_{L,R} = T_{L,max} - T_{L,min}$. All data presented are temperatures in °C.

	Glass A: ARG-1			Glass B: Xr-9			Glass C: AmCm-19		
Participant	GT	UT	CF	GT	UT	CF	GT	UT	CF
PNNL	1033 ± 2	1038 ± 6	1028 ± 5 ^A	947 ± 2	965 ± 5	-	-	1225 ± 5	1226 ± 5 ^A
SRNL	-	1024 ± 5	-	-	-	-	-	1214 ± 5	-
INL	1065 ± 2	1046 ± 2	-	966 ± 3	956 ± 3	-	-	-	-
Monarch	-	1034 ± 4	-	-	970 ± 3	-	-	-	-
CEA	-	1036 ± 2	-	-	-	-	-	1230 ± 2	-
NNL	-	1042 ± 2	-	-	-	-	-	1230 ± 2	-
U. Modena	-	1035 ± 5	1042 ± 5 ^{<i>B</i>}	-	-	-	-	-	1236 ± 5 ^B
	-	_	1062 ± 5 ^A	-	-	-	-	-	-
U. Sheffield	-	_	1033 ± 5^{C}	-	-	-	-	-	1220 ± 5 ^B
	-	_	1040 ± 5 ^{<i>B</i>}	-	-	-	-	-	-
ICT	-	_	-	-	-	-	-	-	-
VSL	-	_	-	-	-	-	-	-	-
T _{L,min}	1033	1024	1028	947	956	-	-	1214	1220
T _{L,max}	1065	1046	1062	966	970	-	-	1230	1236
T _{L.R}	32	22	37	19	14	-	-	16	16
Average	1049	1036	1041	957	964	-	-	1225	1227
St. Dev.	-	6.9	13.0	-	7.1	-	-	7.5	8.1
Average		1040			961			1226	
St. Dev.		11.54			9.26			7.221	

^A C_F determined by XRD method with Rietveld analysis.

 B C_{F} determined by crystal volume method with image analysis.

 $^{C}C_{\rm F}$ determined by crystal number method with image analysis.

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FIG. 12 Scanning Electron Micrographs of (*A*) Spinel Found in Glass A (Captured at 930°C) and (*B*) Zircon Found in Glass B (Captured at 830°C) as well as an Optical Micrograph of Rare Earth Borosilicates Found in Glass C (Captured at 1200°C) During the Round-Robin Study.

ANNEX

(Mandatory Information)

A1. CARE OF THE PLATINUM CRUCIBLES AND TRAYS

A1.1 The condition of the crucibles is critical to achieving meaningful results from the experiments laid out in this procedure. The platinum boats should be cleaned and free of adhering glass or other materials (for example, transition metals). Special care must be taken when handling platinum foil; the more the foil is handled, the higher the occurrence of rips, tears, and holes. If working with platinum foil to form crucibles, it is recommended that the sheet(s) of foil be heat-treated without contact of other platinum at $T \ge 1000^{\circ}$ C

for ≥ 24 hr before contacting other platinum surfaces to prevent Pt-Pt sintering. This bake-out step will result in an inert oxide layer on the surface of the foil that will help prevent the platinum from sticking to itself (which results in tears and holes in the crucibles) and will increase the ability to clean the crucibles. To be satisfactory for $T_{\rm L}$ determinations, the boat, cube, or thimble crucible used in making these measurements should have no holes or cracks in the bottom, side walls, or corners as these can lead to leakage of the glass out of the

crucible during sample heat-treatment. Crucibles should be free of adhering glass or other undissolved materials as these can lead to sample cross-contamination.

A1.2 Cleaning the Boats-Platinum crucibles should be cleaned in concentrated hydrofluoric acid (HF, typically 48 to 50 % by volume) to remove any adhering glass because the HF will attack the silicate network. If HF does not clean the crucible effectively, or if undissolved solids from the glass (for example, transition metal-based precipitates such as spinel) remain adhered to the crucible walls, the platinum can be further cleaned with a cleaning glass or flux that will incorporate these precipitates (for example, low viscosity alkali borate). An ideal cleaning glass is typically one with few components (for example, it is easy to make), a low viscosity, and a low $T_{\rm M}$ to make the process quick. Load the contaminated platinum-ware into a separate, larger crucible of chemical compatibility with the cleaning glass or flux in order to prevent dissolution of the crucible while cleaning. The cleaning glass should be in contact with all of the affected (that is, contaminated) surfaces to achieve adequate cleaning. Ideally, once the cleaning glass has removed all of the transition metals from the crucible walls, the crucible can then be soaked in HF for a second time to remove cleaning-glass residue. The alkali borate flux is water soluble and can be removed, or at least softened, from platinum surfaces by first soaking the platinumware in warm or hot water. The adhering glass can then be softened and removed with a soft brush and then by rinsing in ASTM Type I water.

A1.3 *Reshaping the Crucibles*—Once the residual glass has been removed from the crucible walls, the crucibles can be reshaped using the procedure outlined in 6.1 for the GT method and in 6.2 for the UT method.

A1.4 *Iron Contamination Removal*—Use tongs to place the crucibles into concentrated hydrochloric acid. After a half hour or more, any residual iron that may have been picked up from reforming dies or other sources is dissolved. Upon removal from the acid, rinse the crucible thoroughly with tap water and then ASTM Type 1 water and allow to dry.

APPENDIX

(Nonmandatory Information)

X1. THIS EXHIBIT SHOWS AN EXAMPLE DATA SHEET THAT CAN BE USED TO TRACK THE HEAT-TREATMENTS ON A PARTICULAR SAMPLE

LIQUIDUS TEMPERATURE DATA SHEET								
Glass ID	Reference							
Test Requestor	Phone							
Sample Received	Date							
Special Instructions								
Method Used (GF, UT, CF):	Precision Goal							
PREPARATION								
Sample Prepared by (Name/Date):	Crucible Identification:							
Furnace Identification(s):	Furnace Profile date(s):							
Standard Measured Date/Ref#:								
HEAT TREATMENTS (Record information for each heat treatment.)								
Date/Time Temp. In Date/Time Temp. Out	Sample Analysis & Observation Furnace#							
	7							
	′L							
Primary Crystalline Phase/source data Operator Signature and Date								

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