

# Forensic Glass Examinations

## 1 Scope

### 1.1 Introduction

This document provides guidance for selecting/organizing an analytical scheme for identifying and comparing glass by Geologist-Forensic Examiners within the Trace Evidence Unit (TEU). The size and condition of the samples, as well as the information requested will influence the selected analytical scheme.

The forensic examination of suspected glass is undertaken for investigative and intelligence purposes to:

- determine if an unknown particle is glass;
- determine the compositional class and product type;
- determine if two or more fragments originated from different sources;
- determine the significance of finding two or more glass fragments indistinguishable; and
- determine the cause and nature of breakage.

A comparison involves the recognition and evaluation of class characteristics that associate materials to a group but never to a single source. Only when two or more broken glass fragments physically fit together can it be said that they were once part of the same object. When a difference is found between compared items, the examination may be immediately discontinued and it can be reported that the compared fragments did not originate from the same broken glass source. Refer to *Introduction to Forensic Glass Examination, Initial Examinations of Glass and Collection, Handling and Identification of Glass* by the Scientific Working Group for Materials Analysis for further discussion on these subjects.

### 1.2 Specimens

The various examination techniques described in this guideline apply to most types of glass, including the following: flat glass used for windows, doors, display cases, and mirrors; automotive glass; container glass; tableware glass; optical glass; decorative glass; and specialty glass used for headlamps, cookware, and others.

## 2 Equipment/Materials/Reagents

- Cameras
- Light box equipped with daylight equivalent source
- Micrometer capable of measuring in inches to the fourth decimal place
- Personal protective equipment as needed
- Stereobinocular microscope with minimum magnification of 4 diameters

- Ultraviolet (UV) light source capable of producing short wavelength (nominally 254 nm) and long wavelength (nominally 350 nm) UV light
- Polariscopes
- Petrographic microscope (PLM)
- Additional materials may be used at the discretion of the Geologist/Forensic Examiner.

### **3 Standards And Controls**

Refer to the Refractive Index of Glass by Glass Refractive Index Measuring System (GRIM) and Elemental Analysis of Glass by ICP-OES Procedures for standards and controls used for each analysis technique.

### **4 Sampling**

**4.1** Refer to the Refractive Index of Glass by GRIM, Laboratory Annealing of Glass, and Elemental Analysis of Glass by ICP-OES Procedures for sampling guidance for each analysis technique.

**4.2** In cases where large quantities of glass are received in a sample, a portion of the entire sample may be selected for thickness measurements and fluorescence determination based on a visual inspection of the entire sample.

### **5 Procedures**

**5.1** Glass may be received as suspected broken glass fragments, or may be contained in debris recovered from objects. Thoroughly examine debris for glass fragments using a stereobinocular microscope.

**5.1.1** All suspected glass must first be identified as glass. Glass fragments can be identified using the following properties: it will not deform under pressure; it breaks with conchoidal fracture; it has a vitreous luster; it is non-crystalline; and it is isotropic.

**5.2** Recovered glass (questioned glass) will be evaluated to identify characteristics suitable for comparison prior to comparison to exemplar glass samples. Characteristics not present or expressed in the recovered glass need not be assessed in the exemplar glass. Similarly, characteristics not present or expressed in the exemplar glass need not be assessed in the recovered glass.

**5.3** If enough glass is present and the examination is requested or useful, perform fracture analysis. Refer to the Fractography of Brittle Materials Procedure for a description of glass fracture analysis. No further testing may be necessary after a fractography examination.

**5.4** Assess the physical properties of the glass, including characteristics such as color, type of glass, etc. if they are expressed in the glass and will address the contributor's request. At the discretion of the Geologist/Forensic Examiner, the glass may be photographed.

**5.4.1** Observe the broken fragments for indications of tempering. Tempered glass typically breaks into cube-shaped fragments or "dice." The fracture surfaces may exhibit a frost line. Tempered glass exhibits internal stresses that may be resemble birefringence when observed in cross-polarized light on a polariscope or PLM.

**5.4.2** Using natural light or a light box equipped with a daylight equivalent source, observe the color of the glass fragment on edge. No color may be apparent in small fragments, or even in larger fragments of lightly colored glass. Slight differences in color can be observed by comparing like-sized fragments side-by-side.

**5.4.2.1** Glass fragments are considered to be distinguishable if the observed hue or saturation of color of like-sized fragments is different, or if the hue or saturation of color is different in dissimilarly sized fragments.

**5.4.3** If an original surface is present, assess the glass for fluorescence under short wave and long wave UV light in a darkened room. The tin side of glass manufactured by the float process will fluoresce under short wave UV light. Glass samples may also exhibit an overall fluorescence.

**5.4.4** For comparisons of flat glass specimens, measure the thickness of the fragment with a micrometer if the original surfaces of both the known and questioned glass fragments are present.

**5.4.4.1** When measuring thickness of known glass, measure all fragments with two original surfaces or a minimum of 10 fragments in cases where there are more than 10 fragments with two original surfaces. To adequately assess the variability of the object, measure the thickness across the entire object when possible/available. If the glass measured falls into two or more distinct thicknesses populations, it may indicate the presence of multiple sources of glass in a single sample. Additional thickness measurements may be useful in differentiating these populations.

**5.4.4.2** When measuring the thickness of questioned glass, measure ten fragments with original surfaces that have not been previously disassociated by other properties. If ten fragments with original surfaces are not present, measure all glass fragments with original surfaces. If all of these fragments are distinguishable from the known glass by thickness measurement, additional questioned glass fragments, if present and suitable, will be measured. The total number of glass fragments measured is at the discretion of the Geologist/Forensic Examiner.

**5.4.4.3** The items measured are considered indistinguishable if the questioned item(s) falls within the range of the known glass item. Each questioned glass fragment is compared individually. In cases where the variability of the known glass cannot be adequately assessed, the average of the measured values  $\pm 0.001$ " will be used as the range for the known glass.

**5.5** Optical properties will be measured if assessing the optical properties will address the contributor's request or be useful. Glass that has been heated in a fire may be thermally altered, and therefore the optical properties would be changed. For such samples, laboratory annealing before measuring refractive indices can remove strain introduced as a result of the fire.

**5.5.1** Measure the refractive index of the glass at one or more wavelengths. Refer to the Refractive Index of Glass by GRIM Procedure for a description of measurement of refractive index of glass.

**5.6** When questioned glass is not distinguishable in refractive index from the known glass, both may be annealed to determine whether or not they have similar thermal histories. If the glass may have been thermally altered, annealing before measuring refractive indices will remove strain introduced so that a meaningful comparison may be performed. Refer to the Laboratory Annealing of Glass Procedure.

**5.7** Measure the elemental composition of the glass if the physical properties assessed are the same and the refractive indices are indistinguishable based on the association criteria, if there is sufficient glass present, and if measuring the chemical composition of the glass will address the contributor's request. The elemental composition of ten elements in the glass is routinely measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). Refer to the Elemental Analysis of Glass by ICP-OES Procedure for a description of the preparation and analysis of glass samples by ICP-OES. Other methods of elemental analysis including scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS), or X-ray fluorescence spectrometry (XRF) may be used as a screening test to determine the chemical composition of the glass specimens at the discretion of the examiner.

**5.8** Record all pertinent observations, measurements and instrument data in case notes.

## **5.9 Verification**

Glass associations will be verified by a second qualified Geologist/Forensic Examiner. A glass association is defined as follows:

- 1) When two or more pieces of broken glass physically fit together, the fragments were once part of the same broken object.  
or
- 2) If elemental composition data has been acquired: When the physical properties assessed are the same, the average of multiple refractive index measurements of the questioned items falls within the range of refractive index values of the items from known sources, and the averages of the elemental concentrations of the elements measured falls within the modified  $4\sigma$  interval, the glasses are said to be indistinguishable (see Refractive Index of Glass by GRIM and Elemental Analysis of Glass by ICP-OES).
- 3) If elemental composition data has not been acquired: When the physical properties assessed are the same and the average of multiple refractive index

measurements of the questioned items falls within the range of refractive index values of the items from known sources, the glasses are said to be indistinguishable (see Refractive Index of Glass by GRIM).

All other glass examination results may be verified by a second qualified Geologist/Forensic Examiner.

Verifications will be recorded in Forensic Advantage (FA). Any disagreements between the primary examiner and verifying examiner will be addressed under the FBI Laboratory Operations Manual, Practices for Resolution of Scientific or Technical Disagreement.

## **6 Calculations**

Refer to the Refractive Index of Glass by GRIM, Elemental Analysis of Glass by ICP-OES, and Laboratory Annealing of Glass Procedures for calculation requirements for each analysis technique.

An average thickness is calculated by summing the thickness measurements for a single item and dividing by the total number of thickness measurements for that item.

## **7 Measurement Uncertainty**

**7.1** Refer to the Refractive Index of Glass by GRIM for measurement uncertainty for that technique.

**7.2** The measurement uncertainty of thickness is on the order of  $\pm 0.0002''$ , depending on the micrometer used. Refer to instrument manuals for uncertainty for a particular micrometer. The variation in thickness of flat glass ordinarily does not exceed  $0.1''$ . Thickness variation in curved glass is typically even greater.

## **8 Limitations**

**8.1** Refer to the Refractive Index of Glass by GRIM, Elemental Analysis of Glass by ICP-OES, and Laboratory Annealing of Glass Procedures for the limitations for each analysis technique.

**8.2** The amount of sample and sample adulteration can limit the examination and resulting conclusions.

## 9 Safety

**9.1** Broken glass will be handled while wearing appropriate personal protective equipment.

**9.2** UV light in the range of 254 nm is classified as UVC. Prolonged exposure to UVC light can cause burning of skin, cornea, and conjunctiva, and can also cause nuclear cataracts. Care must be taken to minimize exposure to UVC light. A laboratory coat and opaque gloves will be worn to protect the skin, and use of the UVC light should be severely limited to reduce the potential for damage to the eyes.

**9.3** Eye protection and gloves will be used when breaking glass.

## 10 References

- Koons, Robert D., JoAnn Buscaglia, Maureen C. Bottrell, and Elmer Miller, Forensic Glass Comparisons, Forensic Science Handbook. R. Saferstein (ed), 2002. Prentice-Hall, 2002.
- Glass Refractive Index Determination, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Volume 7, No 1, January, 2005.
- Introduction to Forensic Glass Examination, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Volume 7, No 1, January, 2005.
- Garvin, Elizabeth J., and Koons, Robert D, Evaluation of Match Criteria Used for the Comparison of Refractive Index of Glass Fragments, *Journal of Forensic Sciences*, Volume 56, No 2, March 2011.
- Latkoczy, Christopher et al., Development and Evaluation of a Standard Method for the Quantitative Determination of Elements in Float Glass Samples by LA-ICP-MS, *Journal of Forensic Sciences*, 50(6): 1327-1341, 2005.
- Trejos, Tatiana, et al., Forensic Analysis of Glass by  $\mu$ -XRF, SN-ICP-MS, LA-ICP-MS and LA-ICP-OES: Evaluation of the Performance of Different Criteria for Comparing Elemental Composition, *Journal of Analytical Atomic Spectrometry*, 28: 1270-1282, 2013.
- Introduction to Forensic Glass Examination, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Vol 7, No 1, Jan 2005.

- Initial Examination of Glass, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Vol 7, No 1, Jan 2005.
- Collection, Handling and Identification of Glass, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Vol 7, No 1, Jan 2005.
- Refractive Index of Glass by GRIM, Trace Evidence Procedures Manual (current version).
- Elemental Analysis of Glass by ICP-OES, Trace Evidence Procedures Manual (current version).
- Laboratory Annealing of Glass, Trace Evidence Procedures Manual (current version).
- Chemistry Unit, Metallurgy, Operation of the Thermo QUANT'X X-Ray Fluorescence Spectrometer (current version).
- Chemistry Unit, Metallurgy, Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (current version).
- Chemistry Unit, Metallurgy, Operation of the Bruker M4 Tornado X-Ray Fluorescence Spectrometer (current version).
- FBI Laboratory Safety Manual (current version).

Rev. #	Issue Date	History
5	01/31/19	Changed “will” to “can” in Section 5.4. Changed references of “chemical composition” to “elemental composition” to conform to Department of Justice Uniform Language for Testimony and Reports (ULTR) for the Forensic Geology Discipline and other TEU documents. Changed Section 5.8 Verification to conform to other TEU documents. ICP-OES defined in section 5.6.
6	02/10/2020	Added section 5.2 and renumbered subsequent sections as necessary. Removed ‘or Sample Selection’ from Section 4 title.

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
 Chief

Date: 02/07/2020

Mineralogy Technical  
 Leader

Date: 02/07/2020



# Fractography of Brittle Materials

## 1 Scope

### 1.1 Introduction

This document describes techniques used in the reconstruction of objects broken as a result of brittle fracture and the characterization of certain fracture features in brittle materials as observed through microscopic and macroscopic examination by Geologist/Forensic Examiners within the Trace Evidence Unit (TEU). Brittle materials are particularly well-suited for fractography because there is no distortion caused by the breakage, and objects can be reassembled to their original configuration. Refer to *Glass Fractures* by the Scientific Working Group for Materials Analysis for further discussion on this subject. The techniques to be used in an individual case are chosen to address the request. Not all techniques described in this procedure may be required in every case.

### 1.2 Principle

The reconstruction of objects broken as a result of brittle fracture and/or examination of points of impact and fracture features may yield the following information:

- Determining that broken pieces were once part of the same broken object
- Type of breaking force
- Direction of force
- Angle of incidence
- Type and/or description of object
- Point(s) of impact
- Sequence of impact occurrence

Additional information concerning the mechanism of breakage may also be revealed through examination of broken objects. The references listed in Section 10 can be consulted for procedures for determining additional information.

## 2 Equipment/Materials/Reagents

- Cameras
- Forceps
- Magnifying glass
- No. 2 pencil/Charcoal pencil
- Personal protective equipment (PPE) as needed
- Short wavelength (254 nm) ultraviolet (UV) light source
- Stereobinocular microscope with minimum 4 diameters magnification
- Transparent tape
- White paper/tracing paper

## 3 Standards and Controls

Not applicable.

## **4 Sampling**

Not applicable.

## **5 Procedure**

**5.1** Objects broken as a result of brittle fracture may be reassembled to show that they were once part of the same object, or as an aid in further fractography examinations.

**5.1.1** Place sample identification markings on all pieces that may be used in reassembly.

**5.1.2** Observe surface characteristics, curvature, material type, color, thickness, and fluorescence for glass objects to ensure that all pieces could be from a single object. Sort pieces from different objects as necessary.

**5.1.3** When possible, surface features, fluorescence in glass, and curvature may be used to ensure that they are placed in the same orientation (e.g. top side facing up). Surface features, fluorescence in glass, and/or curvature may not be present in all broken objects.

**5.1.4** Assemble pieces.

**5.1.4.1** Surface features and defects existing before the fracture, where present, will match up across a fracture.

**5.1.4.2** The meshing of pieces can be felt when two pieces will not slip past one another with gentle pressure.

**5.1.4.3** The edges of meshing pieces will be examined to verify that fracture features such as Wallner lines match up across a fracture.

**5.1.4.4** During reassembly, the pieces may be attached to one another with transparent tape.

**5.2** The cause of fracture may be determined. Fractures are caused by thermal stresses, impacts, and bending. Manufacturing defects can also cause fracturing, but are outside the scope of this document.

**5.2.1** Thermal fractures occur when heat is applied to an object unevenly, causing localized expansion or contraction which results in rupture. These fractures may be recognized by curved cracking which often develops a meandering path, cracks perpendicular to the surface, and a symmetrical mirror at the crack origin.

**5.2.2** High velocity impacts may be recognized by the development of a Hertzian cone. Increased velocity of the impact results in cracks radiating from the Hertzian cone, and possibly

the development of concentric cracks.

**5.2.3** Low velocity impacts may be recognized by the absence of a Hertzian cone, although a zone of crushing may be present; cracks radiating from the point of impact; and when enough force is applied, the development of concentric cracks.

**5.2.4** Examine points of impact for residues and remove for further examinations, if necessary.

**5.2.5** Bending may be recognized by a series of cracks which form sub-parallel to each other, and perpendicular to the breaking force.

**5.3** The direction of breaking force in impacts and bending may be determined.

**5.3.1** Perforations of brittle objects by high velocity projectiles will produce a coning or cratering effect with the opening being larger on the exit side. Even when there is little or no loss of material, a ring-shaped crack forms at the point of impact, flaring outward with depth into the material.

**5.3.2** In low velocity impacts, radial cracks initiate opposite the side of the breaking force. Examine the crack face on radial cracks near the point of impact. Use the orientation of Wallner lines to determine the side of crack initiation. Wallner lines near the point of impact on radial cracks will initiate on the side opposite of the breaking force. Wallner lines on concentric cracks near the point of impact may also be used to determine the side of crack initiation, but these cracks initiate on the side of the breaking force. Other fracture features, such as cantilever curl, may be of some utility in determining direction of impact. In tempered or laminated glass, Wallner lines cannot be used to determine the side of crack initiation.

**5.3.3** In bending, cracks form perpendicular to the breaking force. As the object bends, cracks initiate on the convex side of the bend. Use the orientation of Wallner lines to determine the side of crack initiation. Other fracture features, such as cantilever curl, may be of some utility in determining direction of bending force. In tempered or laminated glass, Wallner lines cannot be used to determine the side of crack initiation.

**5.4** A high-speed projectile striking an object at an angle produces a skewed Hertzian cone, shortened on the direction from which the projectile came, and elongated on the exit side.

**5.5** The sequence of breakage can be determined by observing intersecting cracks.

**5.5.1** Only examine cracks which developed as a result of the breakage event.

**5.5.2** New cracks terminate in preexisting cracks.

**5.5.3** If the stress that caused a crack continues after it terminates in a preexisting crack, a new crack may form on the other side of the preexisting crack, but it will jog. Wallner lines and twist hackle on the reinitiation crack are discontinuous with those on the arrested crack even when the jog is small.

**5.5.4** If crack systems from a series of impacts do not intersect, determining the sequence of the impacts is not possible.

**5.6** If desired and feasible, overlay paper on both sides of impact areas and rub with pencil to preserve observations. At the discretion of the Geologist-Forensic Examiner, the object may be photographed.

**5.7** Record all pertinent observations and measurements in case notes.

## **6 Calculations**

Not applicable.

## **7 Measurement Uncertainty**

Not applicable.

## **8 Limitations**

**8.1** Brittle fracture examinations can be severely restricted due to damage of the evidence that could occur from improper collection and preservation at the scene or during shipping.

**8.2** It is usually impractical to reassemble tempered glass objects.

**8.3** Glass objects held tightly in a frame may not exhibit primary Wallner lines perpendicular to the direction of breaking force.

## **9 Safety**

**9.1** Broken glass should be handled while wearing appropriate gloves and eye protection.

**9.2** Ultraviolet (UV) light in the range of 254 nm is classified as UVC. Prolonged exposure to UVC light can cause burning of skin, cornea, and conjunctiva, and can also cause nuclear cataracts. Care must be taken to minimize exposure to UVC light. A laboratory coat and opaque gloves will be worn to protect the skin, and use of the UVC light should be severely limited to reduce the potential for damage to the eyes.

## 10 References

- Thornton, J.I and P.J.Cashman, Glass Fracture Mechanism-A Re-Thinking, *Journal of Forensic Sciences*, 31 1986.
- Koons, Robert D., JoAnn Buscaglia, Maureen C. Bottrell, and Elmer Miller, 2002. Forensic Glass Comparisons, Forensic Science Handbook. R. Saferstein (ed), 2001. Prentice-Hall.
- Frechette D., Failure Analysis in Brittle Materials, Advances in Ceramics, Volume 28; V.; The American Ceramic Society, Westerville, Ohio, 1990.
- Varshneya, Arun K. Fundamentals of Inorganic Glasses, Academic Press, Inc, Harcourt Brace & Company, New York, 1994.
- Glass Fractures, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Volume 7, No 1, January, 2005.
- Quinn, George D., Fractography of Ceramics and Glasses, NIST Special Publication 960-16, National Institute of Standards and Technology, 2007.

Rev. #	Issue Date	History
2	02/07/2018	Updated throughout removing references to TEU where appropriate. Updated Section 1 Scope to include Geologist/Forensic Examiner. Section 1.2 'should' changed to 'can'. Added 'or Sample Selection' to Section 4. Section 5.6 'examiner' changed to Geologist/Forensic Examiner'. Updated title of Section 7. Section 8.1 updated for clarity. Section 9.2 changed should to will.
3	02/10/2020	Section 1.2 reworded to mirror ULTR language. Additional reference added. Removed 'or Sample Selection' from Section 4 title.

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
Chief

Date: 02/07/2020

Mineralogy Technical  
Leader

Date: 02/07/2020

## Geologically-Derived Materials Examinations

### 1 Scope

This document provides guidance for selecting/organizing an analytical scheme for identifying and comparing geologic materials (e.g., soil, rocks, minerals, gemstones), geologically-derived materials (e.g., bricks, concrete blocks, ceiling tile), and unknown materials of suspected geologic origin by Geologist-Forensic Examiners within the Trace Evidence Unit (TEU). Geologic materials, geologically-derived materials, and unknown materials of suspected geologic origin will be collectively referred to in this document as “geologically-derived materials.” These materials lend themselves to identification and comparison utilizing standard geologic/mineralogic techniques and instrumentation. The quantity and condition of the items of evidence, as well as the information requested will influence the selected analytical scheme and the order in which examinations are performed.

Forensic examinations of geologically-derived materials are conducted for investigative and intelligence purposes to:

- determine if two or more geologically-derived materials originated from different sources;
- identify an unknown material;
- determine the origin/end use of geologically-derived materials; and
- determine the significance of finding two or more geologically-derived materials indistinguishable.

A comparison involves the recognition and evaluation of class characteristics that associate materials to a group but never to a single source with the exception of a fracture fit. Only when two or more geologically-derived materials physically fit together can it be said that they were once part of the same broken object (e.g., brick pieces). When a difference is found between compared items, the examination may be immediately discontinued. Refer to *Geoforensics* by Ruffell and McKinley for further discussion.

### 2 Equipment/Materials/Reagents

- 1 and 1½ gauge cover slips
- 10% Hydrochloric Acid (HCl) (reagent grade or higher)
- Balance capable of measuring in grams to the second decimal place
- Calcite, Ward’s Scientific or equivalent supplier of geologic material
- Cameras
- Cargille liquids
- Centrifuge
- Detergent
- Ethyl Alcohol (practical grade or higher)

- Glass microscope slides
- Heat lamp
- Hot plate
- Light box capable of at least providing daylight equivalent light, and equipped with a tungsten lamp
- Magnifying glass
- Microwave oven
- Mortar and pestle
- Muffle furnace
- Munsell Soil Color Charts
- Negative pressure fume hood equipped with HEPA filtration
- Personal protective equipment as needed
- Petrographic microscope with minimum 4x objective, 7.5x oculars
- Probes (e.g., metal, wooden.)
- Rock hammer or equivalent tool
- Sediment texture standard card
- Sieves
- Stereobinocular microscope with minimum magnification of 4 diameters
- Tweezers
- Ultrasonic bath

### **3 Standards and Controls**

**3.1** Spot test sample of calcite reference material with cold 10% HCl by dripping a drop of acid on a clean section of calcite to verify reactivity of acid. If the standard effervesces, the acid is acceptable.

**3.2** Munsell Soil-Color Charts with genuine Munsell® color chips, Munsell Color x-rite Productions, Michigan, 2015 or later.

### **4 Sampling**

The collection and processing of geologically-derived materials from submitted items of evidence can be reviewed in the TEU Evidence Processing Procedures.

### **5 Procedure**

**5.1** Geologically-derived materials may be received in many conditions. Assess the sample of evidence and handle appropriately to minimize deleterious change.

**5.1.1** Centrifuge samples received in liquids (e.g., pond water, stomach contents) to aid in recovery of solid materials, when appropriate.



**5.1.1.1** Place sample in a centrifuge tube.

**5.1.1.2** Place tube in a centrifuge.

**5.1.1.3** Spin sample at 3000 RPM for 5 minutes. Repeat if necessary.

**5.1.1.4** Decant supernatant liquid sample. Solid material is retained in the bottom of the tube.

**5.1.2** When wet samples are received, dry them to ambient conditions. The samples may be air dried, gently heated with a heat lamp, or exposed to microwaves.

**5.1.2.1** When air-drying samples, place open containers in a fume hood and allow to dry.

**5.1.2.2** For more rapid drying, place samples in an open heat-resistant container under a heat lamp and allow to dry.

**5.1.2.3** When using a microwave oven, place samples in an open heat-resistant container in the microwave oven, and heat on the highest setting for five minute increments. Check samples for dryness after each five minute increment, adding more increments as needed until the samples are dry.

**5.1.3** Recovered geologic materials (questioned materials) will be evaluated to identify characteristics suitable for comparison prior to comparison to exemplar geologic materials samples. Characteristics not present or expressed in the recovered geologic materials need not be assessed in the exemplar geologic materials. Similarly, characteristics not present or expressed in the exemplar geologic materials need not be assessed in the recovered geologic materials.

**5.2** If the questioned material is cohesive and of sufficient size, and the examination is requested or useful, perform fracture analysis with known exemplars. If the materials physically fit together and show sufficient correspondence between their macro- and microscopic characteristics to indicate they once comprised a single object, and insufficient disagreement between their macro- and microscopic characteristics to conclude that they originated from different objects, no further testing may be necessary.

**5.3** Examine the sample using a low power magnification (e.g., magnifying glass, stereobinocular microscope), and process to remove materials of interest as needed.

**5.3.1** For intact or partially intact samples, record approximate dimensions, as appropriate, prior to altering.

**5.3.2** If necessary, mechanically separate or subdivide components using probes, tweezers, mortar and pestle, rock hammer, or other tools as appropriate.

**5.3.3** The sample may be ashed to remove organic material (e.g., stomach contents, leaf litter).

**5.3.3.1** Place the sample or a portion of the sample in a crucible.

**5.3.3.2** Place the crucible in a muffle furnace.

**5.3.3.3** Set the temperature of the muffle furnace to between 450°C and 550°C, and heat for at least 8 hours.

**5.4** Assess the dried sample(s) for gross color, texture, quantity, general appearance, and initial identification of the item's components to include anthropogenic and organic materials. At the discretion of the Geologist/Forensic Examiner, the sample(s) may be photographed.

**5.5** Using natural light or a light box under simulated daylight conditions, observe the color of each sample noting color variation and/or mottling, the color of multiple geologically-derived materials if present, and any differences in color between unconsolidated soil and peds/clods if present.

**5.5.1** The color of the samples may be measured by comparison with the Munsell Soil Color Charts.

**5.5.2** Metamerism may be observed using the tungsten lamp.

**5.5.3** Note any mottling, staining, or variation in color from exterior to interior of a sample. If only weathered surfaces are apparent, the sample may need to be further broken until a fresh surface is obtained.

**5.5.4** If the analysis is a comparison, compare the color of the samples to each other. Comparison of like-sized samples side-by-side will reveal slight differences in color. Samples are considered distinguishable if the observed hue, tone, or saturation of color is different.

**5.6** Examine each sample for texture visually, using a stereobinocular microscope or other magnification as necessary. Textural features include grain and ped/clod morphology, particle size distribution, and weathering. In addition to light microscopy, scanning electron microscopy (SEM) can be useful in characterizing particle morphology. Particle size can be determined by a variety of techniques including sieving, sediment texture standard cards, and microscopy (stereobinocular, petrographic, and electron).

**5.6.1** If the analysis is a comparison, compare the texture of the samples to each other. Samples are considered distinguishable if any of the observed textural features between samples are different, with the exception of grain size distribution in unconsolidated materials.

**5.6.1.1** Perform comparisons between similar grain-sized fractions. Differences in grain size distribution between questioned and exemplar samples in unconsolidated materials may be attributed to transfer or may reflect genuine differences in sources. The samples are considered distinguishable when other textural features are different.

**5.7** If it is beneficial for the analysis and there is sufficient material to sub-sample, remove a sub-sample of the material for washing into a crucible or other appropriate container. Sub-samples can be washed to facilitate component identification by polarized light microscopy. If warranted for additional analyses (e.g., clay mineralogy), weigh the sample prior to washing.

**5.7.1** Mix enough detergent in water to form suds when agitated.

**5.7.2** Place sample in dilute detergent and water solution and ultrasonicate for 10 to 15 minutes.

**5.7.3** Decant the supernatant liquid with suspended clays and organic matter into a beaker.

**5.7.4** Repeat steps 5.7.1 through 5.7.3 until supernatant liquid is clear after ultrasonication.

**5.7.5** For comparison examinations, visually compare supernatant liquid side by side, and document any differences noted.

**5.7.6** After removal of the supernatant liquid, the material left behind in the crucible (washed particles) is triple rinsed with water then triple rinsed with ethyl alcohol. The rinsate is recovered into the beaker containing the supernatant liquid.

**5.7.7** The washed portion and supernatant liquid may be air dried or gently warmed by a heat lamp, hot plate, or microwave oven to hasten drying.

**5.8** At the discretion of the Geologist-Forensic Examiner, perform a heavy mineral separation on the washed particles according to the Sample Preparation: Gravity Separation Using Heavy Liquids.

**5.9** Identify the components present and their relative proportions using stereobinocular and petrographic microscopes, or other methods, as needed.

**5.9.1** Materials examined using a petrographic microscope may be mounted on glass slides in various mounting media (e.g., water, Cargille liquids) to facilitate identification.

**5.9.2** If the analysis is a comparison, compare composition between samples. Samples are considered distinguishable if their components are different or if the components are present in different relative proportions. The significance of finding two or more items distinguishable will vary depending upon the rarity of the materials involved.

**5.9.2.1** If the volume of either the known or questioned sample is small (a non-representative sample), minerals present in trace amounts may not be present/observed in the sample. The absence of a phase present in trace amounts in a small sample does not by itself constitute a difference between samples; however conclusions using non-representative samples are more limited.

**5.9.3** If the analysis is a comparison, compare microscopic texture between samples. Samples are considered to be distinguishable when like particles between samples are different texturally (e.g., different morphologies, inclusions).

**5.10** If Portland cement is identified as a phase in a sample of unknown materials for building material by PLM and/or microchemical tests, confirm its presence by XRD.

**5.11** In samples containing Portland cement, the Portland cement may be removed to examine the aggregate.

**5.11.1** Digest a portion of the sample in 10% HCl.

**5.11.2** Decant supernatant liquid.

**5.11.3** Rinse solid material with water.

**5.11.4** Dry solid material in air or with gentle heat. It should be noted that this method will also dissolve any calcite, dolomite, or gypsum contained in the aggregate.

**5.12** If glass fiber is identified, determine whether it is continuous, single strand, matted, woven, etc.

**5.13** Conduct additional analyses at the discretion of the Geologist-Forensic Examiner, depending on the needs of the examination. Some examples are listed below, although other techniques may be used as necessary.

**5.13.1** X-ray diffraction may be useful for identifying minerals below the resolution of a petrographic microscope.

**5.13.2** Pollen identification may be useful in provenance examinations.

**5.13.3** X-ray fluorescence spectrometry may be used to assess chemical composition.

**5.13.4** Scanning electron microscopy can be used to image materials below the resolving power of a petrographic microscope.

**5.14** Record all pertinent observations, measurements and instrument data in case notes.

## 5.15 Verification

Geologically-derived materials associations will be verified by a second, qualified Geologist-Forensic Examiner. A geologically-derived materials association is defined as follows:

- 1) When two or more pieces of a similar geologically-derived material (e.g., block) physically fit together, the compared items were once part of the same object.

or

- 2) When the color, texture and composition are indistinguishable, the possibility that the compared item(s) originated from the same source as the known exemplar cannot be eliminated.

All other geologically-derived materials examinations results may be verified by a second, qualified Geologist-Forensic Examiner.

Verifications will be recorded in Forensic Advantage (FA). Any disagreements between the primary examiner and verifying examiner will be addressed under the FBI Laboratory Operations Manual, Practices for Resolution of Scientific or Technical Disagreement.

## 6 Calculations

Not applicable.

## 7 Measurement Uncertainty

Not applicable.

## 8 Limitations

**8.1** The amount and condition (e.g., adulteration, composition) of an item(s) of evidence can limit the examination(s) and resulting conclusion(s).

**8.2** It is usually not possible to predict the total number of items in a class of materials produced with the same characteristics. In materials with greater compositional and morphological variability (e.g., bricks), a smaller percentage of the total number of items in a class will be indistinguishable than in materials with very little variability (e.g., type E glass fiber).

**8.3** Soil properties vary both across the land and below the land surface as a function of parent material, climate, biological activity, geography, and time, yielding soil that is different from location to location and with depth below the surface. These differences can occur abruptly

or gradually. Therefore the exemplar soils from a specific location must be interpreted to represent only that location, and may not be representative of all soils in the area or soil that may have been present in the past.

**8.4** Due to the possible variations in soil, the boundaries of a homogeneous soil cannot be predicted with absolute certainty. Soil and geologic studies and maps of an area may assist in defining the approximate extent of a homogeneous soil.

## **9 Safety**

**9.1** Some mounting liquids are classified as hazardous and are handled and disposed of in accordance with manufacturer's recommendation or the FBI Laboratory Safety Manual. Avoid contact with skin. Acids can cause burns, throat and eye irritation. Avoid contact with skin, and use in a well-ventilated area. SDS sheets for mounting liquids are maintained with the mounting liquids, and should be consulted for specific precautions for these materials.

**9.2** Eye protection and gloves will be used when crushing specimens of building materials.

**9.3** Building materials such as floor and ceiling tiles, wallboard, skim coats, acoustical plasters, mastic, insulation, and fireproofing may contain asbestos fibers. If a material is suspected to contain asbestos, it must be examined in a negative pressure fume hood equipped with HEPA filtration. Specimens and waste material must be contained in airtight containers when outside the fume hood. These precautions must be followed until it is determined that the material does not contain asbestos. Asbestos containing waste material must be disposed of as a hazardous waste.

## **10 References**

- Ruffell, Alastair, and McKinley, Jennifer, *Geoforensics*, 2008. Wiley and Sons, Ltd.
- Murray, R. C., and Tedrow, J. C. F., *Forensic Geology*, Englewood Cliffs, N.J., Prentice Hall, 1992.
- Munsell Soil Color Charts (current version).
- Sample Preparation: Gravity Separation Using Heavy Liquids, Trace Evidence Procedures Manual (current version).
- Kerr, Paul F., *Optical Mineralogy*, McGraw-Hill, Inc., 1977.

- Mohr, J. Gilbert and Rowe, William P., Fiber Glass, Litton Educational Publishing, Inc., 1978.
- Trace Evidence Unit Evidence Processing Procedures, Trace Evidence Procedures Manual (current version)
- Sample Preparation: X-ray Powder Diffraction, Trace Evidence Procedures Manual (current version)
- Chemistry Unit Standard Operating Procedures (current version)
- FBI Laboratory Operations Manual (current version)
- FBI Laboratory Safety Manual (current version)

Rev. #	Issue Date	History
4	01/31/2019	<p>Document merged with Trace Evidence Procedures Manual Geologic Materials Examinations. Sections 5.1.1 through 5.1.1.4, 5.3.3 through 5.3.3.3, 5.5.2, 5.6.1.1 through 5.9.1, 5.9.2.1, 5.0.3, 5.13 through 5.13.4, 8.3, 8.4, and the first four references copied from the former Trace Evidence Procedures Scope revised to define “geologically-derived materials,” and one reference added.</p> <p>Section 5.4 edited to include reference to additional materials encountered during analysis.</p> <p>Wording added to Section 5.5 to include reference to soil colors.</p> <p>Section 5.6 edited to include SEM analysis and to include reference to soils.</p> <p>Section 5.6.1 edited to include reference to unconsolidated materials.</p> <p>Wording added to Section 5.9.2 to address significance.</p> <p>Section 5.10 edited for clarity.</p> <p>Entire document renumbered.</p> <p>Equipment/Materials/Reagents modified to delete mention of materials not in document, and to add reference to materials added during the merge with Trace Evidence Procedures Manual Geologic Materials Examinations.</p> <p>Section 5.1.2 deleted.</p>
5	02/10/2020	<p>Added section 5.1.3 and renumbered subsequent sections as necessary.</p> <p>Removed ‘or Sample Selection’ from Section 4 title.</p> <p>Removed archived document from references.</p>

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
 Chief

Date: 02/07/2020

Mineralogy Technical  
 Leader

Date: 02/07/2020



# Elemental Analysis of Glass by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

## 1 Scope

### 1.1 Introduction

The concentrations of selected elements in glass serve to chemically characterize the source of the glass. The concentrations of several elements are intentionally controlled by the manufacturers to impart specific end-use properties to a particular glass product. These manufacturer-controlled elements help to chemically characterize a glass fragment by placing it into a particular product use class. The concentrations of trace elements are generally not controlled by the manufacturers. Subtle and distinct differences in the concentrations of manufacturer-controlled elements and uncontrolled trace elements provide a means of differentiating among glasses made by different manufacturers, among glasses from different product lines of a single manufacturer, and over time along an individual production line of glass from a single manufacturer.

### 1.2 Principle

This procedure applies to Geologist-Forensic Examiners who determine the concentrations of aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na), strontium (Sr), titanium (Ti), and zirconium (Zr) in glass fragments in the Trace Evidence Unit (TEU) using of inductively coupled plasma-optical emission spectrometry (ICP-OES). The analysis is performed by dissolving the glass and using the method of ICP-OES for analytical measurements. Quantitative determination of individual element concentrations is achieved by comparing specimens with solutions of matrix matched standards. The procedure can be adapted for the determination of concentrations of additional elements when needed.

### 1.3 Specimens

This procedure is used for the analysis of small fragments of broken glass objects such as: windows, windshields, or containers. When possible, triplicate sub-samples, each weighing 5-8 mg, are selected for analysis from each glass item of interest for dilution to 10 ml of solution. If only 5 ml of the final dilution is to be made, samples as small as 2 mg may be used for each sub-sample. Additional sub-samples may be analyzed at the discretion of the Geologist-Forensic Examiner.

## 2 Equipment/Materials/Reagents

- 1000 µg/ml Scandium Spectrometric Standard Solution (National Institute for Standards and Testing (NIST) (traceable)
- 15-ml disposable polypropylene screw top centrifuge tubes
- 5% hydrochloric acid (HCl) (Optima Grade, equivalent, or higher)
- 49% hydrofluoric acid (HF) (Optima Grade, equivalent, or higher)
- 50-ml disposable polypropylene screw top centrifuge tubes

- Analytical balance (capable of weighing objects between 1 µg and 5000 mg, with ± 1 µg reproducibility, or higher)
- Pipettes or pipette tips and pipetting devices (non-glass, capable of delivering 25 µL - 10 ml)
- Cleaning solution (e.g., Cavicide, Windex)
- Compressed air
- Concentrated hydrochloric acid (HCl) (Optima Grade, equivalent, or higher)
- Concentrated nitric acid (HNO<sub>3</sub>) (Optima Grade, equivalent, or higher)
- Container Glass Reference Material (NIST standard reference material (SRM) 621)
- Convection oven
- Deionized water (18.2 megaohm-cm or higher)
- Erlenmeyer flask
- Ethanol (American Chemical Society (ACS) Reagent Grade, equivalent, or higher)
- Standard Glass Reference Materials (NIST SRM 1831, Schott FGS1 and FGS2)
- Glass Blank, described below, prepared by High Purity Standards or equivalent
- Jeweler's hammer, or steel mortar and pestle, or equivalent
- Kimwipes, Techwipes, or equivalent low lint paper tissue
- Laboratory balance (capable of measuring objects between 1 mg and 100 g with ± 0.1 mg reproducibility, or higher)
- Laboratory coat
- Multi-element glass standard solution, described below as Std #1, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #2, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #3, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #4, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #5, produced by High Purity Standards, or equivalent (calibration standard)
- Nitrile gloves or equivalent
- Plastic sheets or sleeves
- Safety goggles
- Soft bristle brush
- Sonicator
- Thermo Fischer Scientific iCAP 6500 Duo ICP-OES or equivalent with an accompanying personal computer containing the instrument software (e.g., iTEVA), and a printer
- Thermometer
- Tweezers
- Vortex mixer

### 3 Standards and Controls

**3.1** A series of five commercially available multi-element standard solutions and a calibration blank are used to produce calibration curves for every analysis. If the correlation coefficient of the calibration curve ( $r$ ) for any element is less than 0.99, the analysis must be stopped and appropriate remediation measures taken prior to the resumption of the analysis. Appropriate measures could include cleaning the system, changing the tubing, changing the purge solution, checking the system alignment, or other actions as needed.

**3.1.2** The solutions are prepared in a matrix composed of 5% concentrated HCl in deionized water, with 5  $\mu\text{g/ml}$  scandium as an internal standard. Table 1 shows the concentrations of the solutions used to construct the calibration curve. The solutions have a shelf-life of six months to one year. They are stored in tightly sealed containers at room temperature and pressure to maintain stability.

**3.1.3** The quality of new blank and calibration standard solutions must be verified prior to use. This verification consists of analyzing the new solutions on the ICP-OES after calibration with the prior set of blank and calibrations standards. If the concentrations of the new solutions deviate by more than 10% of their expected value, the standards will not be used.

**3.1.4** Negative controls must be analyzed with every analysis. The calibration blank represents a negative control sample. If this specimen produces emission intensities equal to half the emission intensities of Standard #1, the analysis must be stopped and appropriate measures taken prior to the resumption of the analysis. Appropriate measures could include cleaning the system, changing the tubing, changing the purge solution, checking the system alignment, preparing new solutions, or other actions as needed.

**Table 1: Elemental Concentrations of the Standard Solutions ( $\mu\text{g/ml}$ ,  $\pm 0.5\%$ )**

Element	Blank	Std #1	Std #2	Std #3	Std #4	Std #5
Al	0	0.05	0.1	1	10	20
Ba	0	0.01	0.05	0.1	1	2
Ca	0	15	30	45	60	75
Fe	0	0.1	0.5	1	5	10
Mg	0	0.1	0.2	2	10	20
Mn	0	0.01	0.05	0.1	1	2
Na	0	40	60	80	100	120
Sr	0	0.01	0.05	0.1	1	2
Ti	0	0.01	0.05	0.1	1	3
Zr	0	0.01	0.05	0.1	0.5	1

Sc	5	5	5	5	5	5
----	---	---	---	---	---	---

**3.2** Standard glasses of known chemical composition, such as NIST SRM 1831, NIST SRM 621, FGS 1, and FGS 2 are stored at ambient temperature and pressure in separate closed containers in the glass preparation area to prevent deleterious change. Glass standards maintained in this fashion have an indefinite shelf-life.

**3.2.1** Each analytical set is analyzed with appropriate standard glass samples which are used as positive control samples for that analytical run. The positive control's response will be assessed against the certified and published values for a particular control and the average values from the validation.

**3.2.1.2** Triplicate samples of one or more glass standards, such as SRM 621, SRM 1831, FGS 1, FGS 2, or others appropriate for the evidence glass type, are analyzed with each case in the same manner as evidentiary samples to check the analytical precision and accuracy of the computed results.

**3.2.1.3** Each standard glass measured will be assessed against the control charts for the method determined from the validation. Mean concentration values have been established for each of the glass standards using 15 samples, analyzed over five days. From these analyses, a standard deviation has been established in Table 2. A control is acceptable if the calculated mean value is within three standard deviations ( $\pm 3SD$ ) of the control chart mean, and the relative standard deviations (RSDs) meet the criteria listed above. If the value of the control falls between  $\pm 2SD$  and  $\pm 3SD$  this may be indicative of systemic problems with the instrument or procedure that need to be addressed.

**Table 2: Control Chart Values**

Element	Mean Measured Concentration, %				Standard Deviation			
	SRM 1831	SRM 621	FGS 1	FGS 2	SRM 1831	SRM 621	FGS 1	FGS 2
Al	0.62625	1.47257	0.14872	0.68863	0.03049	0.07839	0.00554	0.06389
Ba	0.00339	0.09280	0.00450	0.01991	0.00020	0.00497	0.00018	0.00186
Ca	6.01236	7.77289	6.22194	5.76230	0.27961	0.41200	0.21241	0.54098
Fe	0.06152	0.03116	0.05771	0.26568	0.00344	0.00822	0.00215	0.02496
Mg	2.17507	0.16749	2.44195	2.26301	0.10913	0.00856	0.08850	0.20336
Mn	0.00134	0.00184	0.00465	0.02158	0.00010	0.00012	0.00019	0.00200
Na	10.0890	9.47519	10.2725	9.51088	0.48881	0.51055	0.37675	0.90502
Sr	0.00937	0.01057	0.00602	0.02570	0.00048	0.00054	0.00021	0.00247
Ti	0.01127	0.00778	0.00702	0.03169	0.00055	0.00044	0.00030	0.00303
Zr	0.00482	0.00702	0.00530	0.02447	0.00046	0.00050	0.00033	0.00219

**3.2.1.4** When precision (measured as RSD) among the standard glass replicate measurements is  $>10\%$  for elements present at readily measurable levels, appropriate measures are taken to

determine the cause of the discrepancy. When the measured concentrations of several elements in a standard glass have relative standard deviations  $>10\%$ , the digest solutions will be reanalyzed. Digestion of additional standard glass samples may be necessary.

**3.3** Each analytical set is analyzed with a digestion blank which is used as a negative control sample for that analytical run. Triplicate blank samples will be prepared with each sample set (See Section 5.1.6). The negative control's response will be assessed. Values greater than half the intensity of Calibration Standard #1 are indicative of contamination during sample preparation or pipetting errors. Data for an analytical run with high digestion blank values may still be used for comparison purposes, but only for data gathered within that analytical run.

**3.4** The calibration of the analytical balances and pipettes is verified with every use and the values are recorded for each case. The calibration of the laboratory balance is checked by using 5 mg and 10 mg weights. The calibration of the pipettes is checked by weighing an appropriate volume of deionized water delivered by the pipette on a laboratory balance before use. The results are recorded. If the value measured differs from the stated value by  $>10\%$ , the balance or pipette must not be used.

**3.5** The quality of new hydrofluoric acid, hydrochloric acid, and scandium internal standards must be checked prior to use. Prepare and run a set of three digestion blank samples by following the instructions at 5.1.6 through 5.1.19, although it is not necessary to analyze standards, samples, or additional blanks. Values greater than half the intensity of Calibration Standard #1 are indicative of contamination in the new reagents. If high values are present, the reagents must be re-prepped and analyzed to confirm the result. Reagents returning high values after at least two checks must not be used.

## **4 Sampling or Sample Selection**

**4.1** If possible, several samples should be selected from each item to represent the range of potential compositions of the glass. When sufficient glass is available, at least three duplicate specimens will be chosen per source.

**4.2** Surface fragments should be avoided if possible because of the potential for contamination from surface coatings or layers with a different composition than the bulk glass (e.g., tin on the float surface).

**4.3** Five to eight milligrams of glass per replicate is considered ideal when producing 10 ml of solution. Two to five milligrams of glass may be used when more glass is unavailable, but these samples must not be diluted to more than 5 ml solution volume.

## **5 Procedures**

### **5.1 Sample Preparation and Analysis**

**5.1.1** Prior to preparing any samples, thoroughly clean the laboratory bench surfaces and all tools/equipment to be used with a cleaning solution and wipe with a low lint material to minimize the potential for contamination.

**5.1.2** Wash each glass item separately by soaking fragments for 30 minutes in concentrated HNO<sub>3</sub>. Rinse three times with deionized water and three times with ethanol. Dry in an oven set to 80°C. Prepare triplicate samples of the appropriate standard glass samples in the same manner. After the samples have been cleaned, handle the fragments using tweezers, gloved hands, or other clean tools.

**5.1.3** Run the internal calibration routine on the analytical balance before use. Save the printout of the results in the case records. To check the calibration and to demonstrate a lack of drift in the balance during use, weigh and record the weights of 5 and/or 10 mg weights at the beginning and end of the weighing session. Drift greater than 0.01 mg may indicate a problem with the reproducibility of the balance, and will necessitate re-weighing the samples.

**5.1.4** Break the glass samples as necessary. To further break the glass, contain a glass fragment by placing it in the cavity of a clean, steel mortar and pestle set. Use the pestle to break the fragment. The crushed glass will be contained in the cavity by the removable metal sleeve. Carefully clean the set using a soft bristle brush and compressed air between each use. Alternately, place the fragment between two sheets of clean, thick plastic and rap the glass sharply with a jeweler's hammer (or equivalent) to crush it. Carefully remove the broken fragments from between the plastic with tweezers. Place the plastic in the glass trash receptacle. Refer to Section 9 for safety guidelines prior to breaking glass.

**5.1.5** Weigh each sample to the nearest 0.01 mg and print out the results. Place each glass sample weighed in individual 15-ml centrifuge tubes. For items where there is sufficient glass to prepare triplicate sub-samples, the first sub-sample measured is identified by the sample identifier followed by the letter "a". Similarly, subsequent sub-samples are identified by the sample identifier followed by the next letter ("b," then "c," ...).

**5.1.6** Add 500 µl of 49% HF to each sample and standard glass control sample tube, and to each of three empty 15-ml centrifuge tubes, which will serve as digestion blanks. Refer to Section 10 for safety guidelines prior to the use of HF.

**5.1.7** Place the uncapped tubes in an oven set to 80°C. Remove the tubes from the oven after 2 hours. Sonicate the sample tubes briefly and return them to the oven until dry (typically 24 to 36 hours).

**5.1.8** Remove the tubes from the oven and let them cool. To produce 10 ml of solution, carefully add 500 µl of concentrated HCl, 9.45 ml of deionized water, and 50.0 µl of scandium internal standard solution to each tube. To produce 5 ml of solution, carefully add 250 µl of concentrated HCl, 4.725 ml of deionized water, and 25.0 µl of scandium internal standard solution to each tube in that order. 10 ml of solution will be produced when the glass fragment weighed ≥ 5 mg prior to dissolution. 5 ml of solution will be prepared when the glass fragment weighed < 5 mg prior to dissolution. Check the calibration of the pipette(s) by weighing an appropriate volume of deionized water delivered by the pipette on a laboratory balance before use.

**5.1.9** Tightly cap the tubes and vortex the contents of each tube for 15 to 20 seconds. Return the tubes to the 80°C oven for one hour.

**5.1.10** Remove the tubes from the oven and briefly vortex their contents. Allow the samples to stand for at least 8 hours to ensure complete dissolution.

**5.1.11** Enter the sample weights, volumes, and location in the autosampler into the iTeva Analyst software used to control the instrument.

**5.1.12** Vortex the sample tubes to mix the contents.

**5.1.13** Place the sample tubes into the autosampler of the ICP-OES for analysis. The calibration standards are analyzed first, then the standard glass samples are analyzed, the dilution blank is analyzed next, and finally the case specimens are analyzed. Samples can be randomized (e.g., 2c followed by 3a followed by 1b, etc.) or analyzed sequentially (e.g., all “a” subsamples, followed by all “b” subsamples, etc.).

**5.1.14** Use a solution of 5% HCl as the purge solution.

**5.1.15** New calibration curves may be generated in the course of a sample analyses at the discretion of the Geologist/Forensic Examiner.

**5.1.16** Clean the torch assembly and replace the tubing on the pump and autosampler as needed. See the instrument manual for further guidance. The tubing may be replaced and the torch cleaned more frequently at the discretion of the Geologist-Forensic Examiner.

**5.1.17** Start the ICP-OES following the guidance in the instrument manual.

**5.1.17.1** Turn on radio frequency (RF) generator and plug in exhaust fan. Wait at least 30 minutes.

**5.1.17.2** Turn on the chiller set to 20° C. Wait at least one hour.

**5.1.18** Start the analysis using the method for glass.

- Open ESI and iTEVA software.
- Turn on plasma.
- Initialize system through the ESI CI window.
- Open <Analyst> in iTEVA.
- Add glass weights and correction factor.
- Run autosession.

**5.1.19** Print a report of the results.

## **5.2 Instrumental Conditions**

This analysis is performed using a Thermo Fischer Scientific iCAP 6500 Duo ICP-OES.

### **Analysis Preferences:**

Sample Options                      #Repeats:                      3

	Delay Time:	0.0 seconds		
	Sample Flush Time:	22 seconds		
Source	Analysis mode:	Speed		
	Sample Introduction:	Nebulizer		
	Plasma View:	Radial		
Analysis Maximum	Low WL Range:	Axial 15	Radial 15	
Integration Time (sec)	High WL Range:	Axial 5	Radial 8	
Calibration Mode	Concentration			
Trailing Full Frame	Intelli-Frame:	Yes		
Options	Max Integration Time (sec):	30		
	WL Range:	Low		
	View:	Radial		

**Source Settings:**

Nebulizer Pump:	Flush Pump Rate (rpm):	38
	Analysis Pump Rate (rpm):	38
	Pump Relaxation Time (sec):	0
	Pump Tubing Type:	Tygon Orange/White
	RF Power:	1150 W
	Nebulizer Flow:	0.57 L/min
	Auxiliary Gas:	0.8 L/min

**Analytical Wavelengths:**

Al	396.152 (nm)
Ba	455.403
Ca	315.887
Fe	259.837
Mg	285.213
Mn	260.569
Na	818.326
Sr	407.771
Ti	338.376
Zr	343.823
Sc	361.384

Preferences may be altered at the discretion of the Geologist-Forensic Examiner. Any changes to the analysis conditions must be recorded in the case notes.

**5.3 Interpretation of the Analytical Results**

**5.3.1** Following the recommendations of Trejos et al (2013), a modified  $4\sigma$  confidence interval is used as the comparison criterion for the comparative analysis of glass fragments by ICP-OES. If the average elemental concentration for any element in the item being compared falls outside of the modified  $4\sigma$  confidence interval for any element in an exemplar sample, the items are considered distinguishable.

**5.3.2** If measured elemental concentrations are between the limit of detection and the limit of quantitation of the instrument, measured concentration values are unreliable and may produce



extremely high RSDs. In this case, reanalysis and/or re-preparation of the samples is not useful. While it is possible to report the presence of an element if the concentration of the element is between the limit of detection and the limit of quantitation, the concentration will not be reported.

**5.3.3** The detection limits of this method vary slightly from day to day. Approximate method detection limits have been stated in the validation records for the Thermo Fischer Scientific iCAP 6500 Duo ICP-OES. These values may be used as a guide, but a better approximation can be determined for each particular case when needed.

## **6 Calculations**

A modified  $4\sigma$  confidence interval is calculated by taking either the measured standard deviation or 3% of the average for each element, whichever is greater, and multiplying it by four. The confidence interval for an element is the average value of the elemental concentration  $\pm$  the modified  $4\sigma$ .

## **7 Measurement Uncertainty**

Not applicable.

## **8 Limitations**

**8.1** RSDs may be unacceptably high in specimens containing less than 3 mg of glass.

**8.2** Analysis of glass using ICP-OES is destructive. ICP analysis will not be possible if it is necessary to preserve all of the glass.

## **9 Safety**

**9.1** Glass digest solutions are classified as hazardous materials and must be handled and disposed of in accordance with procedures set forth in the FBI Laboratory Safety Manual.

**9.2** Personal protective equipment (PPE) must be worn when handling mineral acids, particularly Hydrofluoric Acid (HF), including: gloves, safety glasses, and a laboratory coat. HF is corrosive to all body tissues and bone. Extreme care must be exercised in the presence of this acid. Prior to first use, all personnel handling HF must complete HF Training and successfully pass the HF Quiz provided by the Health, Safety, and Security Unit. While handling HF, a second person who has completed and passed HF training must be present.

**9.3** Outside venting of exhaust gases from the ICP instrument and from the oven used for removal of silicon fluorides during glass specimen dissolution is maintained.

**9.4** Breaking glass can cause glass fragments to be ejected in unpredictable trajectories.

Use caution to break the glass in a way that minimizes blowback. Broken glass can cause cuts and damage to eyes and exposed skin. PPE must be worn when handling or breaking glass including: gloves, safety glasses, and a laboratory coat.

## 10 References

- Abollino, O., et al., Determination of Zirconium, Barium, Lanthanum, Aluminum, Sodium, Hafnium and Fluorine in Fluorozirconate Glasses: Development of Different Dissolution Procedures and Analytical Techniques, *Fresenius Journal of Analytical Chemistry*, 343: 482-487, 1991.
- Casoli, Antonella and Piero Mirti, The Analysis of Archaeological Glass by Inductively Coupled Plasma Optical Emission Spectroscopy, *Fresenius Journal of Analytical Chemistry*, 344:104-108, 1992.
- Hickman, D. A., Elemental Analysis and the Discrimination of Sheet Glass Samples, Metropolitan Police Forensic Science Laboratory Report No. 22, September 1982.
- Koons, et al., Classification and Discrimination of Sheet and Container Glasses by Inductively Coupled Plasma-Atomic Emission Spectrometry and Pattern Recognition, *Journal of Forensic Sciences*, 33(1): 49-67, 1988.
- Koons, et al., Comparison of Refractive Index, Energy Dispersive X-Ray Fluorescence and Inductively Coupled Plasma Atomic Emission Spectrometry for Forensic Characterization of Sheet Glass Fragments, *Journal of Analytical Atomic Spectrometry*, 6: 451-456, 1991.
- Koons, Robert D. and JoAnn Buscaglia, The Forensic Significance of Glass Composition and Refractive Index Measurements, *Journal of Forensic Sciences*, 44(3): 496-503, 1999.
- Koons, Robert D. and JoAnn Buscaglia, Interpretation of Glass Composition Measurements: The Effects of Match Criteria on Discrimination Capability, *Journal of Forensic Sciences*, 47(3): 505-512, 2002.
- Latkoczy, Christopher et al., Development and Evaluation of a Standard Method for the Quantitative Determination of Elements in Float Glass Samples by LA-ICP-MS, *Journal of Forensic Sciences*, 50(6): 1327-1341, 2005.
- Trejos, Tatiana, et al., Forensic Analysis of Glass by  $\mu$ -XRF, SN-ICP-MS, LA-ICP-MS and LA-ICP-OES: Evaluation of the Performance of Different Criteria for Comparing Elemental Composition, *Journal of Analytical Atomic Spectrometry*, 28: 1270-1282, 2013.
- Wolnik, Karen L., et al., Analysis of Glass in Product Tampering

Investigations by Inductively Coupled Plasma Atomic Emission

- Spectroscopy With a Hydrofluoric Acid Resistant Torch, *Journal of Analytical Spectrometry*, Volume 4, February 1989.
- FBI Laboratory Safety Manual (current version)
- Thermo Fisher Scientific iCAP 6500 Duo ICP-OES Operation Manual.

Rev. #	Issue Date	History
2	02/07/2018	<p>Updated throughout removing references to TEU where appropriate.</p> <p>Updated examiner title to Geologist/Forensic Examiner in Scope in Sections 1.2 and 1.3, minor wording changes to accommodate examiner title change.</p> <p>Updated Section 2.</p> <p>Added wording to Section 3.1 regarding appropriate remediation measures.</p> <p>Updated wording in Section 3.1.2 specifying Table 1 shows concentrations of standards. Also, clarified expiration dates.</p> <p>Section 3.1.3 wording updated for clarification.</p> <p>Updated Section 3.2 for clarity regarding shelf-life.</p> <p>Section 3.3 removed requirement that weights be recorded on the weight sheet.</p> <p>Added 'Sample Selection' to Section 4 and in Section 4.3 specified per replicate.</p> <p>Updated wording in Section 5.1.1, 5.1.13, 5.1.15, and 5.1.16 for clarity.</p> <p>For Section 5.1.4, added information about soft bristle brush and compressed air.</p> <p>For Section 5.1.8, specified to produce solution, reagents/standard must be added in that order.</p> <p>Section 5.1.10 changed from overnight to at least 8 hours.</p> <p>Updated Section 5.1.18 to remove requirement for method being printed and placed in case file as it is in this SOP.</p> <p>In Section 5.1.19, removed specific software name.</p> <p>Calculations in Section 5.3.1 moved to Calculations section.</p> <p>Updated Section 5.3.2 and 5.3.3 for clarity.</p> <p>Updated Section 9 for clarity.”</p> <p>'Specimen' changed to 'sample' throughout document.</p> <p>'Documented' changed to 'recorded' throughout document.</p> <p>Updated references in Section 10.</p>
3	02/10/2020	<p>Section 4.1 changed “item” to “source.”</p> <p>Changed Sections 5.1.4 and 5.1.8 to active voice.</p> <p>Changed 5.3.1 to conform to other TEU documents.</p> <p>Added sections 3.1.3, 3.3, and 3.5 and renumbered following sections as necessary.</p> <p>Changed “the glass digestion” to “a calibration” in sections 3.1 and 3.1.4.</p> <p>Changed “may” in section 4.3 to “must.”</p> <p>Requirement to use a weight sheet removed from section 5.1.8.</p> <p>Grammar corrected in 5.1.11.</p> <p>Updated the Health, Safety, and Security Unit name in section 9.2.</p>

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
Chief

Date: 02/07/2020

Mineralogy Technical  
Leader

Date: 02/07/2020

## Sample Preparation: X-ray Powder Diffraction

### 1 Scope

This document provides the procedure for the sample preparation for X-ray powder diffraction (XRD) used by Geologist/Forensic Examiners within the Trace Evidence Unit (TEU). In X-ray powder diffraction, the material to be examined is reduced to a very fine powder and placed in a beam of monochromatic x-rays. Each particle of the powder is a tiny crystal or assemblage of smaller crystals, oriented at random with respect to the incident beam. The result is that every set of lattice planes will be capable of reflection. The material of interest must be crystalline or have a regularly repeating atomic structure, and should have been previously described using the Geologic Materials Examinations and the Geologically Derived Materials Examinations Procedures.

### 2 Equipment/Materials/Reagents

- Acetone, laboratory grade (or equivalent)
- Agate mortar and pestle
- Chemical resistant gloves
- Deionized water
- Ether, laboratory grade (or equivalent)
- Ethyl alcohol, laboratory grade (or equivalent)
- Glass slides
- Haskris model R100 Chiller unit or equivalent
- International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF)
- Laboratory coat
- PANalytical X'Pert Pro MPD X-ray Diffractometer (XRD) or equivalent
- Sieve set, to include 200 mesh sieve
- Additional materials may be used at the discretion of the Geologist/Forensic Examiner

### 3 Standards and Controls

Not applicable.

### 4 Sampling or Sample Selection

**4.1** The collection and processing of crystalline materials from submitted items of evidence can be reviewed in the TEU Evidence Processing Procedures.

**4.2** At the discretion of the Geologist/Forensic Examiner, the entire sample or component(s) or mixes of components of interest may be analyzed. These materials are prepared for identification as necessary at the discretion of the Geologist/Forensic Examiner. Individual

sub-samples may not be representative of the entire specimen. Sub-samples are chosen based on the need to identify a particular component.

## **5 Procedure**

### **5.1 Isolated Samples or Samples Which May Be Removed From Their Substrate**

**5.1.1** The sample or portion of a sample to be analyzed may be ground if necessary. To grind a sample or portion of a sample, transfer the portion to be analyzed to an agate mortar.

**5.1.1.2** Grind the sample or portion of the sample with an agate pestle. Grinding method is determined as appropriate for sample at the discretion of the examiner.

**5.1.1.2.1** Dry grinding – the sample is ground between mortar and pestle in air.

**5.1.1.2.2** Wet grinding – the sample is ground between mortar and pestle in a carrying/lubricating medium. Medium should be easily volatilized, for example, acetone, water, or ethyl alcohol. Use enough medium to wet the sample and add more as necessary to keep the sample wet while grinding.

**5.1.1.2.2.1** Take the sample to dryness when grinding is complete.

**5.1.2** The sample or portion of a sample to be analyzed may be sieved if necessary. For most samples the portion of the sample which passes through a 200 mesh sieve is most appropriate for optimal XRD signal. Size fraction used is at the discretion of the Geologist/Forensic Examiner and is dependent on the individual sample.

**5.1.3** Mount the sample in a holder. The holder used is determined at the discretion of the Geologist/Forensic Examiner as appropriate for the sample.

#### **5.1.3.1 Low Background Slide**

Evenly distribute the sample on a low background slide in the area illuminated by X-ray beam when the sample is analyzed.

**5.1.3.1.1** Wet deposition.

**5.1.3.1.1.1** Suspend the sample in a carrying medium. Medium should be easily volatilized, for example, acetone, water, or ethyl alcohol.

**5.1.3.1.1.2** Place the suspension on a slide.

**5.1.3.1.1.3** Evaporate the carrying medium.

**5.1.3.1.2** Dry deposition. Sprinkle the sample onto a slide.

### **5.1.3.2 Well Holder**

**5.1.3.2.1** It is preferable to load the sample from the back side of the well holder.

**5.1.3.2.1.1** Remove the back of the sample holder.

**5.1.3.2.1.2** Place the holder front side down on a clean glass slide.

**5.1.3.2.1.3** Pour the sample into the well and compress with a clean glass slide.

**5.1.3.2.1.4** Replace the backing to the holder.

**5.1.3.2.1.5** Invert the holder, and remove the slide from the front of the holder, being careful not to disturb the surface of the sample.

**5.1.3.2.2** To front load the well holder:

**5.1.3.2.2.1** Pour the sample into the well holder.

**5.1.3.2.2.2** Flatten the exposed side of the sample by gently compressing with a glass slide.

## **5.2 Samples Which May Not Be Separated From Their Substrate**

**5.2.1** Remove portion of sample and attached substrate, or use entire sample with substrate for those materials that will fit on the sample holder.

**5.2.2** Affix sample and substrate to sample holder.

## **6 Calculations**

Not applicable.

## **7 Measurement Uncertainty**

Not applicable.

## **8 Limitations**

XRD analysis is limited to crystalline substances or materials with regularly repeating atomic structure.



## 9 Safety

**9.1** Some carrying/lubricating media are classified as hazardous, and will be handled and disposed of in accordance with manufacturer's recommendations or the FBI Laboratory Safety Manual.

**9.2** Universal precautions will be used and at least the minimum appropriate personal protective equipment (PPE) such as laboratory coats and protective gloves will be worn when handling samples.

## 10 References

- Cullity, B. D., Elements of X-Ray Diffraction, Reading, Massachusetts, Addison-Wesley Publishing Company, Inc., 1978.
- Jenkins, Ron, and Robert L. Snyder, Introduction to X-Ray Powder Diffractometry, New York, New York, John Wiley & Sons, Inc., 1996.
- Skoog, Douglas A., and Donald M. West, Principles of Instrumental Analysis, 2nd edition, Philadelphia, Pennsylvania, Saunders Golden College Series/Holt, Rinehart and Winston, 1980.
- FBI Laboratory Safety Manual (current version).
- Geologic Materials Examinations, Trace Evidence Procedures Manual (current version)
- Geologically Derived Materials Examinations, Trace Evidence Procedures Manual (current version)
- Trace Evidence Unit Evidence Processing Procedures, Trace Evidence Procedures Manual (current version)

<u>Rev. #</u>	<u>Issue Date</u>	<u>History</u>
0	07/10/06	Original issue.
1	02/07/18	Updated title removing reference to TEU and throughout document where appropriate to reflect change from unit-specific to discipline-specific. Added Geologist/Forensic Examiner to Scope, Section 1 and throughout document where appropriate. Section 4 Calibration deleted, document renumbered. Section 4 updated heading to add "Sample Selection" and 7 retitled. Section 4.1 updated to reflect current title of document and update Section 4.2 to provide option for analysis of entire sample. Section 5 introductory sentence added and edits made throughout this section for clarity. Sections 9.1 and 9.2: 'will' substituted for 'should'. Section 9.2: 'Personal protective equipment' substituted for 'protective attire'. References updated in Section 10 and throughout document.

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
Chief

Date: 02/06/2018

Mineralogy Technical  
Leader

Date: 02/06/2018

**QA Approval**

Quality Manager

Date: 02/06/2018

# Laboratory Annealing of Glass

## 1 Scope

### 1.1 Introduction

This document provides for the laboratory annealing of glass particles by Geologist/Forensic Examiners within the Trace Evidence Unit (TEU). In glass manufacturing, annealing is the process of reducing residual strain in glass by controlled heating and cooling. The technique described in this document applies to flat glass used for windows, doors, display cases, and mirrors; automotive glass; optical glass; and glass objects that have been in a fire.

The thermal history of glass fragments is a useful property in determining glass source classifications. When questioned glass is not distinguishable in refractive index (RI) from the known glass, both may be annealed in the Laboratory to determine whether or not they have similar thermal histories. Because annealing alters the optical properties of a glass fragment, in most cases, RI should be measured before laboratory annealing. After the sample is annealed in the Laboratory, its RI can be measured again. RI generally increases after laboratory annealing and the magnitude of change in RI ( $\Delta$ RI) may be used to classify fragments as originating from tempered or non-tempered sources.

Laboratory annealing is also useful in the determination and comparison of refractive indices of glass samples that have been subjected to fire (e.g. arson cases). A glass object that has been heated in a fire may be thermally altered, and therefore the RI of the glass would be changed. This change is unpredictable, and is not typically uniform across a glass object. For such samples, laboratory annealing before measuring refractive indices will remove strain introduced as a result of the fire so that a meaningful comparison may be performed.

### 1.2 Definitions

**1.2.1** The *annealing point* is the temperature at which the strain in glass will be relieved. See Table 1 for the approximate annealing points of glass types commonly seen in casework.

**1.2.2** The *annealing range* spans the upper limit of the annealing region, slightly above the annealing point, through the strain point.

**1.2.3** Stresses engendered in a piece of glass by heating and cooling may be *temporary* until the glass cools to a lower temperature at which it acquires *ordinary permanent strain*.

**1.2.4** The *softening point* is the minimum viscosity that the worked mass of glass must have before being allowed to stand on its own (or it will deform under its own weight).

**1.2.5** The *strain point*, or the lower limit of the annealing region, is the point below which no additional permanent strain will be introduced in the glass. The strain remaining in the glass is directly proportional to the cooling rate prior to reaching the *strain point*.

**Table 1. Common Glass Types and Their Approximate Viscosity Data**

Glass Code	Type	Strain Point °C	Annealing Point °C	Softening Point °C
0080	Soda Lime (Tubing)	395	435	630
0281	Soda Lime (General Purpose)	490	530	707
7250	Borosilicate (Baking Ware)	485	530	780
7740	Borosilicate (General Purpose)	520	565	820

Corning Glass Works, Corning, NY, 1957

## 2 Equipment/Materials/Reagents

- Ceramic spot plate or equivalent
- Forceps
- Insulated gloves
- Laboratory coat
- Programmable muffle furnace or equivalent
- Safety goggles

## 3 Standards And Controls

Not applicable.

## 4 Sampling or Sample Selection

**4.1** The procedures for the collection and processing of glass from submitted items of evidence can be reviewed in the TEU Evidence Processing Procedures.

**4.2** Glass fragments selected to be annealed should be large enough to split in two pieces: one to determine the pre-annealed RI value and one to determine the post-annealed RI value. Smaller fragments may be annealed at the discretion of the Geologist/Forensic Examiner.

## 5 Procedure

**5.1** Place each glass fragment to be annealed into an individual well in a ceramic spot plate(s) or equivalent.

**5.2** Note the location of each fragment. Labeling the spot plates with a “permanent” marker is not a sufficient labeling method as the ink will ash at high temperatures.

**5.3** Load the samples into the muffle furnace. When space allows, all fragments to be compared will be annealed simultaneously.

**5.4** Close the door of the muffle furnace.

**5.5** Place the power switch to the ON position.

**5.6** Program the muffle furnace according to the following conditions:

**5.6.1** Ramp the temperature in the furnace up to the set point at a rate no greater than 25°C per minute. The set point should be chosen to be above the *strain point* and below the *annealing point* typical for glass of the type being annealed (see Table 1). 525°C is sufficient for most glasses commonly encountered in forensic casework.

**5.6.2** Hold the temperature at the set point for at least 30 minutes.

**5.6.3** Set the cooling rate to slowly cool the glass at approximately 1°C/minute through the suspected *strain point* (see Table 1). Other cooling rates may be programmed at the discretion of the Geologist/-Forensic Examiner. When the *annealing point* is not known with any great accuracy, the slow cooling should continue to 375°C, which is below the *strain point* for most glasses commonly encountered in casework.

**5.6.4** Below the suspected *strain point*, the cooling rate can be set at a faster rate at the discretion of the Geologist/-Forensic Examiner, up to 5°C/minute. Alternately, the muffle furnace may be turned off and allowed to cool undisturbed with the door closed. Do not open the door of the muffle furnace until the temperature control reads less than 200°C.

**5.7** Run the program.

## **6 Calculations**

Not applicable.

## **7 Measurement Uncertainty**

Not applicable.

## **8 Limitations**

**8.1** Annealing changes the RI of sample.

**8.2** Some glass fragments may be too small to recover without the risk of losing them.

**8.3** The use of the other annealing protocols such as the Locke "short schedule" can result in lower  $\Delta$ RI values than those obtained using longer annealing schedules.

**8.4** Upon annealing, heat-strengthened glass has a  $\Delta$ RI intermediate between that of non-tempered and tempered glass. Therefore, it is not always possible to classify glass type using  $\Delta$ RI

alone.

**8.5** Extremely small glass fragments can be lost during annealing.

**8.6** Glass with an unusual composition may have a higher *strain point* and *annealing point* than the glasses listed in Table 1. Glasses with unusual compositions may not be fully annealed even when heated to 525°C.

## 9 Safety

**9.1** Appropriate eye protection and gloves will be used when handling broken glass.

**9.2** Eye protection and gloves will be used when breaking glass.

**9.3** Always wear insulated gloves when handling hot materials.

## 10 References

- Koons, R.D., Buscaglia, J., Bottrell, M.C., and Miller, E., Forensic Glass Comparisons, Forensic Science Handbook. R. Saferstein (ed), Prentice-Hall, 2002.
- Glass Refractive Index Determination, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Vol. 7, No. 1, January, 2005.
- Introduction to Forensic Glass Examination, Scientific Working Group for Materials Analysis, *Forensic Science Communications*, Vol. 7, No. 1, January, 2005.
- Trace Evidence Unit Evidence Processing Procedures, Trace Evidence Procedures Manual (current version)
- FBI Laboratory Safety Manual (current version).
- Handbook of Glass Manufacture, Volume II, Third Edition, McMaster, H.A. (ed), Glasstech, Inc., 1984.
- Marcoullier, J. M., A Revised Glass Annealing Method to Distinguish Glass Types, *Journal of Forensic Sciences*, Vol. 35, No. 3, May 1990.
- Properties of Selected Commercial Glasses, Corning Glass Works, Corning, NY, 1957.
- Locke, J., Sanger, D.G., and Roopnarine, G., The Identification of Toughened

Glass By Annealing, *Forensic Science International*, Vol. 20, 1982.

- Locke, J., Winstanley, R, Rockett, L.A., and Rydeard, C., A Comparison of Long and Short Schedules for the Annealing of Glass Particles, *Forensic Science International*, Vol. 29, 1985.

Rev. #	Issue Date	History
0	10/12/11	Original issue.
1	02/07/18	Updated throughout removing references to TEU where appropriate. Updated Section 1 Scope to include Geologist/Forensic Examiner and throughout document when appropriate. Deleted Section 4 Calibration and document renumbered. Updated new Section 4 to add 'Sample Selection' and minor edits. 'Specimen' changed to 'sample' throughout document. Section 5.3: "Q and K" deleted. Updated Sections 9.1 and 9.2 to change 'should' to 'will'. References updated in Section 10 and throughout document.

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
Chief

Date: 02/06/2018

Mineralogy Technical  
Leader

Date: 02/06/2018

**QA Approval**

Quality Manager

Date: 02/06/2018



## Refractive Index of Glass by GRIM

### 1 Scope

This document provides the procedures for determining the refractive index (RI) of microgram sized glass fragments at up to three wavelengths using the Foster and Freeman, Ltd. Glass Refractive Index Measuring System (GRIM 3) by Geologist/Forensic Examiners within the Trace Evidence Unit (TEU). RI is the ratio of the velocity of speed of light in one media compared to the speed of light in a vacuum. It varies according to the wavelength of the light and the temperature of the medium, but its value in a particular glass at a set wavelength and temperature is a function of the composition of the glass and its thermal history. RI provides excellent discrimination among glasses, and is the most commonly measured property in forensic glass comparisons. Refer to *Glass Refractive Index Determination* by the Scientific Working Group for Materials Analysis (SWGMA) and ASTM E1967-11a, *Standard Test Method for the Automated Determination of Refractive Index of Glass Samples Using the Oil Immersion Method and a Phase Contrast Microscope* for further information.

Using the GRIM 3 method, a glass fragment is immersed in an appropriate reference liquid and observed at the wavelength of interest while the temperature is electronically varied until the match point temperature is reached. The match point temperature is automatically recorded. The match point temperature can be determined at multiple wavelengths, typically  $n_D$ ,  $n_C$ , and  $n_F$ .

### 2 Equipment/Materials/Reagents

- 1 or 1½ gauge coverslips
- Alcohol (methanol, ethanol, or isopropyl alcohol, any grade)
- Detergent such as sodium hexametaphosphate (or equivalent)
- Forceps
- Glass microscope slides, 76mm x 19mm
- Glass RI reference materials
  - National Bureau of Standards (NBS) melt 9012
  - Bundeskriminalamt (BKA) K5 (Schott Optical Glass)
  - Additional standards at the discretion of the Examiner
- GRIM 3
- Hammer mill
- Hot stage capable of maintaining a temperature to  $\pm 0.2^\circ\text{C}$  or better
- Interference filters, wavelengths approximately  $n_D$ ,  $n_C$ ,  $n_F$
- Kimwipes, Techwipes, or equivalent lint-free paper tissue
- Locke Scientific standard reference glasses (Locke B1 through B4, Locke B6 through B12, Locke A1 through A5, Locke C1 and Locke C2, or equivalent)
- Locke Scientific Silicon oil A, B, or C or equivalent
- Nitric acid ( $\text{HNO}_3$ , any grade)
- Personal Protective Equipment, as needed
- Phase Contrast Microscope with minimum 10x magnification
- Probes (e.g., metal, wooden)
- Ultrasonic bath

- Water

### 3 Standards and Controls

**3.1** Standard glasses of known RI, such as NBS melt 9012 and BKA K5 Schott Optical Glass, are mounted on a glass microscope slide in the appropriate oil. An appropriate oil is similar in RI to the standard glass at the temperature and wavelength of interest. The mounted glass standards are then analyzed by GRIM 3 according to section 2 of the GRIM 3 Glass Refractive Index Measurement System Instruction Manual and User Guide.

**3.2** Standards are stored at room temperature and pressure, and maintained in separate containers to prevent contamination. Properly maintained standards have an indefinite lifetime.

**3.3** Accuracy of the GRIM 3 system is assured by proper alignment of the instrument. The alignment of the instruments is checked prior to each use. See the Trace Evidence General Microscopy Techniques for instructions on microscope alignment.

**3.4** The GRIM 3 will be calibrated: yearly when the instrument is in use; prior to use if not calibrated within the previous 12 months; or if the measurement of the standards exceeds accepted tolerances and cleaning and re-alignment fail to correct this situation.

**3.5** Locke Silicon oil (A, B, or C) will be calibrated for the temperature range of interest. The oil chosen is based upon the expected RI of the glass to be analyzed. A minimum of three standard reference glasses will be used when calibrating the Locke A and B oils. Only two standard reference glasses are available for the RI range of the Locke C oil, and both must be used when calibrating the Locke C oil. Additional oils (e.g. Dow Corning 710 or 550 oil) may be calibrated for use at the discretion of the examiner.

**3.5** Calibrate the GRIM 3 according to the guidelines presented in the GRIM 3 Glass Refractive Index Measuring System User Manual, Sections 2 and 9.

**3.5.1** A calibration curve is constructed for each silicon oil of interest at the  $n_D$ ,  $n_C$ , and  $n_F$  wavelengths.

**3.5.2** Collect six measurements for each of the standard reference glasses at the temperatures of interest. Do not use the Locke Scientific Standard Glass B5.

### 4 Sampling or Sample Selection

**4.1** For known source items, several samples should be selected to represent the range of RI measurements of the glass (Sandercock, 2000; Garvin and Koons, 2011).

**4.1.1** When sufficient glass is available, select at least seven fragments from the known sample to mount on individual glass microscope slides. If there are less than seven fragments in a known sample, make at least one glass microscope slide mount per fragment.

**4.1.2** Measure at least 21 different suitable edges, with an approximately equal number of

measurements made per slide produced. To avoid bias, select the first suitable edges found upon scanning the slide.

**4.1.2.1** Suitable edges are bright, thin, clean, smooth and sharp (see the GRIM 3 Glass Refractive Index Measuring System User Manual, Sections 2 and 7). The edge traces provide an indicator of acceptability. Fragments with poor edge traces will be assessed as to their suitability.

**4.2** When measuring RI of questioned glass, measure all suitable fragments that have not been previously disassociated by other tests, or a minimum of ten fragments in cases where there are more than ten suitable fragments that have not been previously disassociated by other tests. If all of these fragments are disassociated by RI measurement, additional glass, if present and suitable, will be measured. The total number of glass fragments measured is at the discretion of the examiner.

**4.2.1** Suitable glass fragments are those of sufficient size to crush for measurement of fresh edges. Additional factors such as the presence of coatings or contaminants may limit suitability. The determination of suitability of each glass fragment is left to the discretion of the Geologist/Forensic Examiner.

**4.2.2** If more than ten glass fragments are recovered from a questioned item, but less than ten glass fragments are suitable for analysis, the reason(s) why the fragments are unsuitable will be recorded in the case notes. If less than ten glass fragments are recovered and any of them are unsuitable for analysis, the reason(s) why the fragments are unsuitable will be recorded in the case notes.

**4.2.3** Measure all suitable edges, or a minimum of ten edges in cases where there are more than ten suitable edges.

## **5 Procedures**

**5.1** Turn on the computer, monitor, and GRIM 3 power and place the interference filter of the wavelength of interest over the field diaphragm. Allow electronics to warm up for approximately one hour.

**5.2** Check that the microscope optics and hot stage are clean and free of oil. Clean if necessary. See Trace Evidence General Microscopy Techniques.

**5.3** Arrange the microscope for optimum illumination and phase contrast. To ensure maximum contrast, make sure the annular illumination ring from the condenser is properly aligned with the phase contrast shift plate located within the objective by viewing the superimposition at the back focal plane of the objective. This can be accomplished in a number of ways, the most convenient of which are the use of a Bertrand lens or a phase centering telescope. See Trace Evidence General Microscopy Techniques.

**5.4** Clean a glass RI slide with water or alcohol and a clean, dry, lint-free wipe.

**5.5** Put a drop of the appropriate Locke Scientific silicon oil A, B, or C on the cleaned

slide. For the majority of soda-lime silicate glasses, Locke Scientific B is the appropriate oil. Locke Scientific C is the appropriate oil for most borosilicate glasses. Locke Scientific A is appropriate for very high refractive index glasses.

**5.6** Select a clean particle previously determined to be glass (see Forensic Glass Examinations) and place it in the oil on the slide. If needed, fragments may be cleaned prior to analysis.

**5.6.1** Clean fragments by soaking them in alcohol, a detergent solution followed by a water rinse, or nitric acid followed by a water rinse. Fragments may also be cleaned in an ultrasonic bath in alcohol, or in a detergent solution followed by a water rinse. Following cleaning, dry thoroughly.

**5.7** Crush the fragment(s) in situ with a clean metal probe or equivalent. Glass fragments can also be crushed in a clean hammer mill or equivalent and transferred to the glass microscope slide. Fragments too small to be crushed by these methods are inappropriate for analysis.

**5.8** Heat slide for approximately 15 minutes at 100°C to drive off volatile impurities in the oil.

**5.9** Cover sample with a clean coverslip. In necessary, coverslips may be cleaned using alcohol and a lint-free wipe.

**5.10** Create a case according to the GRIM 3 Glass Refractive Index Measuring System User Manual, using the unique FBI case and item identifiers.

**5.11** Measure the refractive index of the glass standards (NBS 9012 and BKA K5), followed by the glass specimens from the case. If measurement of the case specimens exceeds one day, the glass standards must be measured each day prior to obtaining measurements for case specimens.

**5.11.1** Insert a prepared mount of a glass sample into the hot stage mounted on the phase contrast microscope stage and allow the sample and hot stage to equilibrate.

**5.11.2** Check the alignment of the microscope and adjust if necessary. See Trace Evidence General Microscopy Techniques.

**5.11.3** Locate the first suitable fragment found upon scanning the slide, and position an edge box on the edge. The GRIM 3 can measure up to four edges simultaneously. A focus indicator appears as a three digit number in the bottom right hand corner of the video window. The focus of the fragment must be adjusted so that the focus indicator is at its maximum prior to a measurement. When analyzing multiple edges, if the focus indicator cannot be maximized for all edges simultaneously, then only edges that can be maximized may be measured in a single run.

**5.11.4** Adjust the temperature of the hot stage so that the temperature is slightly above the match point of the glass. Two degrees above the match point is recommended.

**5.11.5** Analyze the glass fragments according to section 2 of the GRIM 3 Glass Refractive

## Index Measuring System User Manual.

**5.11.5.1** Analyze at least five fragments each of two known glass standards (NBS 9012 and BKA K5) at the wavelength of interest prior to each use of the GRIM 3.

**5.11.5.1.1** The average value of each standard must be within  $\pm 0.00005$  of the accepted value. Individual measurements cannot exceed  $\pm 0.0001$  of the accepted value.

**5.11.5.1.2** If the average value of either of the standard glass falls outside of the accepted tolerance ( $\pm 0.00005$ ), or the individual measurements exceed  $\pm 0.0001$  of the accepted value, the GRIM 3 will be cleaned and re-aligned and the standard glasses will be reanalyzed.

**5.11.5.1.3** If the average measurement of either of the glass standards falls outside of the accepted tolerance ( $\pm 0.00005$ ), or the individual measurements exceed  $\pm 0.0001$  of the accepted value, and cleaning and re-alignment fail to correct this, the instrument will be recalibrated.

**5.11.5.1.4** If the average measurement of either of the glass standards falls outside of the accepted tolerance after recalibration, the data collected cannot be used for comparison against any other data collected during a different analysis session.

**5.11.5.2** For known glass specimens, measure at least 21 different suitable edges, with an approximately equal number of measurements made per slide if more than one slide was produced.

**5.11.5.3** For questioned glass specimens, measure all suitable edges, or a minimum of ten suitable edges in cases where there are more than ten suitable edges. If there are less than three suitable edges, the specimen is inappropriate for analysis using the GRIM 3.

**5.11.6** Repeat the above procedure if desired at additional wavelengths by using the appropriate filters.

**5.12** At the completion of the analysis, include the results in the case notes.

**5.13** If the analysis is a comparison between known source(s) and questioned glass fragments, the resultant range of refractive index values from known broken glass source(s) versus the average of multiple measurements of the questioned glass fragments are used as the comparison criteria. When the average of multiple refractive index measurements of the questioned items falls within the range ( $\geq$  minimum and  $\leq$  maximum) of refractive index values of the items from known source(s), the glasses are said to be indistinguishable.

**5.14** If the analysis is a comparison between two or more questioned glass fragments, range overlap of multiple measurements of each questioned glass fragments is used as the comparison criteria. When the ranges of one questioned glass fragment ( $\geq$  minimum and  $\leq$  maximum) and another questioned glass fragment ( $\geq$  minimum and  $\leq$  maximum) overlap, the glasses are said to be indistinguishable.

## 6 Calculations

An RI average is calculated by summing the RI values for a single item at one wavelength and dividing by the total number of RI measurements for that item at that wavelength.

## 7 Measurement Uncertainty

The calculated precision of the GRIM 3 is based on the reported precision of the hot stage (0.2°C) and is between 0.00004 and 0.00007 at all wavelengths.

## 8 Limitations

**8.1** The precision of the method, as determined by multiple measurements of homogenous standard glass samples, is better than the variation of RI in most sample glasses. Typical values of uncertainty in measured indices are in the fifth decimal place.

**8.2** Fragments that do not provide a good edge for index determination can result in degraded precision. The quality of the edge trace can be an indicator of the acceptability of the measurement (see GRIM 3 Glass Refractive Index Measuring System User Manual, page 38). RI values from poor quality fragments should not be reported.

## 9 Safety

Eye protection and gloves will be worn when breaking glass items.

## 10 References

- ASTM International. ASTM E1967-11a. Standard Test Method for the Automated Determination of Refractive Index of Glass Samples Using the Oil Immersion Method and a Phase Contrast Microscope. West Conshohocken, Pa.: ASTM International, 2011.
- Garvin, EJ and Koons, RD. Evaluation of Match Criteria Used for the Comparison of Refractive Index of Glass Fragments. Journal of Forensic Sciences March 2011;56(2):491-500.
- Foster and Freeman, Ltd. GRIM 3 Glass Refractive Index Measurement System Instruction Manual and User Guide. July, 2009.
- Laboratory Division Safety Manual (current revision).
- Locke Scientific. Reference Glasses and Silicone Oils for Refractive Index Determination.

Sandercock, PML. Sample Size Considerations for Control Glass in Casework. Canadian Society Forensic Science Journal 2000;33:169-178.

- Scientific Working Group for Materials Analysis (SWGMA). Glass Refractive Index Determination. Forensic Science Communications January, 2005;7(1), <http://www.fbi.gov/hq/lab/fsc/backissue/jan2005/standards/2005standards7.htm>, accessed 1/25/2018.
- Trace Evidence General Microscopy Techniques, Trace Evidence Procedures Manual (current version)

Rev. #	Issue Date	History
1	11/02/15	<p>Section 2 Updated list.</p> <p>Section 3 Reworded for clarity.</p> <p>Section 4.1 Added statement about cleaning and realigning prior to redoing calibration.</p> <p>Section 4.2 Reworded for clarity, added possibility of using additional oils.</p> <p>Section 5.1.2 Clarified number of analyses.</p> <p>Section 5.2 Reworded for clarity.</p> <p>Section 5.2.1 Reworded for clarity.</p> <p>Section 5.2.3 Added to clarify number of required measurements.</p> <p>Section 6 Revised and renumbered for clarity and transparency.</p> <p>Section 7 Added calculation of average RI.</p> <p>Updated references.</p> <p>Updated for FA, changing “specimen” to “item” when appropriate.</p>
2	02/07/18	<p>Updated throughout removing references to TEU where appropriate.</p> <p>Added Geologist/Forensic Examiner to the Scope in Section 1 and throughout document where appropriate.</p> <p>In Section 1, added clarification regarding RI ratio.</p> <p>Removed Calibration Section 4 and renumbered. Text previously appearing in Calibration section added to Section 3.</p> <p>Added ‘Sample Selection’ to new Section 4.</p> <p>‘Recorded’ substituted for ‘documented’ throughout document.</p> <p>References updated in Section 10 and throughout document.</p>

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
 Chief

Date: 02/06/2018

Mineralogy Technical  
 Leader

Date: 02/06/2018

**QA Approval**

Quality Manager

Date: 02/06/2018



## Sample Preparation: Gravity Separation Using Heavy Liquids

### 1 Scope

Soil samples typically contain multiple mineral species. For the purpose of identification, it is often advantageous to separate soils into their component parts. One method for accomplishing this is to separate specimens based on the specific gravity of the individual minerals. This document describes a procedure for the processing of soil samples using gravity separation in a heavy liquid by Geologist/Forensic Examiners within the Trace Evidence Unit (TEU)

### 2 Equipment/Materials/Reagents

- 5 ml microtube (cryogenically safe)
- Bromoform (Reagent grade)
- Ethanol (any grade)
- Sample splitter
- Containers (glass, ceramic, plastic, other appropriate material)
- Plastic container with a tight fitting lid
- Pasteur pipette
- Gloves
- Forceps
- Laboratory coat
- Liquid nitrogen in cryogenically safe container
- Plate, flat (glass, ceramic, other appropriate material)
- Safety goggles
- Stiff paper or other appropriate material

### 3 Standards and Controls

Not applicable.

### 4 Sampling or Sample Selection

A split of the washed fraction of the soils is used for gravity separation. Refer to the Geologic Materials Examinations Procedure. The sample may be split using either a splitter or coning and quartering.

**4.1.1** If the sample is split using microsplitter, pour sample through a clean microsplitter and use one half for heavy liquid separation, retaining the second half for microscopy or other testing.

**4.1.2** If sample is split using coning and quartering:

**4.1.2.1** Pour washed sample onto a flat surfaced object such as a porcelain plate or a sheet of glass so that it forms a cone.

**4.1.2.2** Insert a stiff yet flexible piece of paper (e.g. a business card) straight down into the center of the cone such that approximately half of the sample is on each side of the cone. Slide the card to the side, pushing half the sample aside.

**4.1.2.3** Repeat step 4.1.2.2 across both piles with the card at right angles to the original split. The sample is now in four piles.

**4.1.2.4** Take one quarter of the sample (one of the piles) and return it to the sample container.

**4.1.2.5** Take the opposite quarter of the sample and return it to the sample container also. This material is one split.

**4.1.2.6** Take the two remaining quarters and place them into another sample container. This material is the second split.

**4.1.2.7** Use one of the splits for heavy liquid separation, retaining the second half for microscopy or other testing.

## **5 Procedure**

**5.1** Take one split of the sample and place it into a cryogenically safe 5 ml microtube.

**5.2** Place approximately 1 ml of bromoform into the microtube and cap the microtube.

**5.3** Gently swirl the sample in the bromoform.

**5.4** Using a Pasteur pipette, wash down the sides of the microtube with bromoform, and recap the microtube.

**5.5** Once the sample in bromoform has settled (approximately 5 minutes), immerse the bottom portion of the microtube in liquid nitrogen to slightly above the level of the heavy fraction until the liquid nitrogen stops boiling vigorously, approximately 5 seconds. The top portion of the bromoform contains the light fraction of the sample and should remain liquid.

**5.6** Uncap the microtube, and pour the liquid bromoform containing the light fraction into a container.

**5.7** Wash down the sides of the tube with additional bromoform to remove any remaining light minerals, and pour the liquid into the container used in step 5.8. Repeat this step as

necessary to achieve separation.

**5.8** Allow the bromoform containing the heavy fraction to thaw and then pour the bromoform containing the heavy minerals into a second container.

**5.9** Wash down the sides of the tube with ethanol to remove any remaining heavy minerals and pour the liquid into the container used in step 5.8. Repeat this step as necessary to remove any remaining heavy minerals from the microtube.

**5.10** Leave the containers with the light and heavy fractions in a fume hood until the bromoform has evaporated. Once the bromoform has evaporated, put each fraction in separate labeled sample containers, such as a small round plastic box. Cap the containers.

## **6 Calculations**

Not applicable.

## **7 Measurement Uncertainty**

Not applicable.

## **8 Limitations**

**8.1** Some components of a soil, such as asphalt containing materials, are soluble in bromoform. If it is necessary to identify those materials, this procedure may not be appropriate.

**8.2** Some soil samples may be so small that processing them by this procedure is not advantageous.

## **9 Safety**

**9.1** Bromoform is a known carcinogen with acute oral toxicity to kidneys, the nervous system, liver, and upper respiratory tract. It is a skin and eye irritant. It is readily absorbed through skin contact and through vapor inhalation.

**9.2** Bromoform must be handled in a fume hood with adequate exhaust ventilation.

**9.3** Universal precautions will be used when handling bromoform, to include lab coat, goggles and chemical resistant gloves.

**9.4** At atmospheric pressure, liquid nitrogen boils at -196°C or -32°F and is a cryogenic

fluid which can cause rapid freezing on contact with living tissue and may lead to frostbite. Liquid nitrogen must be handled in insulated dewers and while wearing insulated gloves. Avoid all contact with skin.

**9.5** As liquid nitrogen evaporates, it displaces oxygen in the atmosphere and may act as an asphyxiant. Liquid nitrogen must only be handled in a well ventilated space.

**9.6** Refer to the most current revision of the FBI Laboratory Safety Manual and appropriate MSDSs for additional information and guidance on hazards and handling.

## 10 References

- International Union of Pure and Applied Chemistry (IUPAC) *Compendium of Chemical Terminology, 2nd edition, "the Gold Book", "Coning and Quartering in Analytical Chemistry,"* compiled by A. D. McNaught and A. Wilkerson, Blackwell Scientific Publishing, Oxford, 1997.
- Geologic Materials Examinations, Trace Evidence Procedures Manual (current version)
- FBI Laboratory Safety Manual (current version)

Rev. #	Issue Date	History
0	02/07/13	Original issue.
1	02/07/18	Updated throughout removing references to TEU where appropriate; added Geologist/Forensic Examiners to the Scope in Section 1. Section 4 Calibration section deleted and document renumbered. Added Sample Selection to new Section 4. Updated title of Section 7. Clarified wording in Section 8. Section 9.3 'should' to 'will'. References updated in Section 10 and throughout document.

**Approval**

Redacted - Signatures on File

Trace Evidence Unit  
Chief

Date: 02/06/2018

Mineralogy Technical  
Leader

Date: 02/06/2018

**QA Approval**

Quality Manager

Date: 02/06/2018