6.2 Examination and Comparison of Glass Samples

6.2.1 Glass Screening

6.2.1.1

Observe and compare macroscopical and microscopical characteristics of glass fragments, including color, tint, texture, presence of coatings, and contour of glass. If sides are parallel, measure the thickness with a micrometer and check for fluorescence with an ultraviolet light. In general, flat glass fragments cannot be differentiated with respect to their thicknesses if their thickness ranges are within 0.15 mm.

Note: Measurement of thickness is for comparison of a Questioned to a Known and is not a "measurement that matters"; therefore, this procedure does not require traceability and verification of the micrometer.

6.2.1.2

Observe isolated small particles with polarizing microscope to determine if they are isotropic. Large and small particles may be observed with fluorescence microscope to detect fluorescent properties, if any.

6.2.1.3

Any large pieces of glass can be compared with remaining evidence to determine the possibility of a fracture match between the Known and the Questioned glass.

6.2.2 Refractive Index analysis using Foster + Freeman GRIM3

Refer to user's manual for appropriate use of instrument. Basic sample and instrumentation preparation steps include:

- Prepare sample of crushed reference glass in Locke Scientific Oil A, B, or C or equivalent on clean glass slide under a glass coverslip. Possible methods include crushing in a clean mortar, crushing using glass slides or a paper packet, or crushing the glass in oil using a metal spatula.
- Insert slide into the hot stage
- Optimize phase contrast by the following actions. Adjust telescope lens of right eyepiece until a bright orange circle appears in focus. Center the bright ring in the shadow of the dark ring by pushing and turning the spring-loaded black toggle bars located posterior to the stage.

6.2.2.1 Quality Assurance for GRIM3

6.2.2.1.1 Calibration

A calibration curve must be established for each oil to be used for casework in each calendar year prior to analysis of casework samples, when any new oil is going to be used for casework, after major instrument service, after software updates, and/or when indicated by the Standard Reference Material data.

A Standard Reference Material should be used to verify the calibration curve.

Print the new calibration and file it with the other calibration records.

6.2.2.1.2 Standard Reference Material (SRM)

6.2.2.1.2.1

The Standard Reference Material is a glass sample with a certified refractive index.

6.2.2.1.2.2

The SRM should be a sample that is not used in the calibration curve.

6.2.2.1.2.3

QA/QC and Detecting Trends

The refractive index of the SRM shall be collected every day casework is analyzed before any casework data is obtained. This assures that the GRIM3, hot stage, and camera are working, the correct filter is in place, and the oil's refractive index properties have not changed. Results of the SRM should be compared to the expected RI of that glass and to previous results as needed/warranted. If measurements fall outside of 0.00010 of the expected RI, action shall be taken. These actions can include preparing a new sample, using new oil, checking the temperature of the hot stage, or recalibrating the oil.

6.2.2.1.2.4

Save all SRM data (electronic and/or hard-copy).

6.2.2.1.2.5

The use of an SRM allows for data taken on separate days to be compared.

6.2.2.2 Case samples

- Obtain the RI at the match temperature of several edges of known glass samples. The amount of known sample dictates the number of edges used, but the recommended number is at least 10 edges. Edge counts of samples to be averaged are recommended to be 50 or higher; however, some samples do not produce edge counts this high. The analyst has discretion to not use outliers in obtaining the RI.
- Obtain the RI at the match temperature of several edges of questioned glass samples. The amount of questioned sample dictates the number of edges used, but the recommended number is at least 8 edges. Edge counts of samples to be averaged are recommended to be 25 or higher, with a minimum of 10. The analyst has discretion to not use outliers in obtaining the RI.
- With respect to refractive index, the known glass is:
    - **Included** as a possible source of the questioned glass if:
        - the refractive index ranges of known and questioned sources overlap, or
        - the average refractive index of known glass is at or within .00010 of the average refractive index of questioned glass
    - **Excluded** as a possible source of the questioned glass if:
        - the refractive index ranges of known and questioned sources do not overlap, and
        - the average RI of known glass is at or more than .00020 of the average RI of questioned glass.
    - **Inconclusive** as a possible source of the questioned glass if:
        - the refractive index ranges of known and questioned sources do not overlap, and
        - the average RI of known glass is between .00010 and .00020 of the average RI of questioned glass.

6.2.3 Glass Elemental Analysis

6.2.3.1 Introduction

The use of a sensitive elemental analysis method yields high discrimination among sources of glass and may assist in classification of the end-use product type. The methods available to the Forensic Science Division for elemental analysis include scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) and micro X-ray fluorescence (μ-XRF).

6.2.3.2 SEM-EDS

6.2.3.2.1

SEM-EDS is a nondestructive elemental analysis technique based on the emission of characteristic X-rays following the excitation of the specimen by an electron beam. Simultaneous multi-elemental analysis is typically achieved for elements of atomic number six or greater. Specimens are mounted and placed into the instrument chamber and subjected to an electron beam. The characteristic X-rays emitted by the

specimen are detected using an energy dispersive X-ray detector and displayed as a spectrum of energy versus intensity.

Qualitative analysis is accomplished by identifying elements present in the specimen based on their characteristic X-ray energies. Semi-quantitative analysis is accomplished by comparing the relative area under the peaks of characteristic X-rays of certain elements. Spectral and elemental ratio comparisons of the glass specimens are conducted for source discrimination or association.

SEM-EDS analysis of glass may discriminate glass samples based on differences in major elemental compositions. It also may discriminate glass samples based on the presence, sequence, and/or thickness of coatings.

Samples with two parallel sides may be examined utilizing SEM-EDS, which is located at the Lansing Laboratory. Please use: **Appendix 6.2 B for SEM/EDS Examination Lansing Laboratory** worksheet

Samples should be mounted float side up on SEM stubs with carbon tape. Because the precision of EDS is highly dependent on geometry, it is necessary that the samples have two parallel sides, in order to assure that beam-sample-detector geometry is maintained. Samples without two parallel sides cannot be accurately examined using this method.

Due to the improved limits of detection of μ-XRF compared to SEM-EDS, SEM-EDS is not the preferred method of bulk analysis of glass. However, using the described methods, discrimination of some samples is possible.

6.2.3.2.2

Samples should be run in variable pressure mode to prevent sample charging. The Operator should select an appropriate accelerating voltage and working distance. Each analysis should encompass at least 100 live seconds.

6.2.3.2.3

Questioned and known glass SEM-EDS analysis should be performed at least five times for each sample in an alternating pattern, i.e. one repetition of the questioned sample followed by a repetition of the known sample, etc.

6.2.3.2.4

Raw elemental data for the following elements is then calculated for the following ratios: Na/Al, Mg/Al, Na/Mg, Fe/Na, Fe/Sn, Ca/Na.

6.2.3.2.5

The standard deviation of the elemental ratios of repeated analyses of the same sample are then calculated and a range of the greater of 5% or three standard deviations of the mean is calculated.

6.2.3.2.6

For inclusion: All of the questioned elemental ratios should fit within the calculated 5% or 3 SD range of the known sample. All of the known elemental ratios should fit within the calculated 5% or 3 SD range of the questioned sample as well.

For exclusion: Two of the elemental ratios of the questioned sample should fall outside the calculated 5% or 3 SD range of the known sample.

An inconclusive result can occur if only one of the questioned elemental ratios falls outside the range for the known sample. In this case, the analysis should be repeated.

6.2.3.3 u-XRF

6.2.3.3.1

µ-XRF is a nondestructive elemental analysis technique based on the emission of characteristic X-rays following the excitation of the specimen by an X-ray source using capillary optics. Simultaneous multi-elemental analysis is typically achieved for elements of atomic number eleven or greater. Specimens are mounted and placed into the instrument chamber and subjected to an X-ray beam. The characteristic X-rays emitted by the specimen are detected using an energy dispersive X-ray detector and displayed as a spectrum of energy versus intensity.

Qualitative analysis is accomplished by identifying elements present in the specimen based on their characteristic X-ray energies. Semi-quantitative analysis is accomplished by comparing the relative area under the peaks of characteristic X-rays of certain elements. Spectral and elemental ratio comparisons of the glass specimens are conducted for source discrimination or association.

µ-XRF analysis of glass may discriminate glass samples based on differences in major, minor, and some trace elemental compositions. Samples with or without parallel sides and of sufficient size (based on the size of the sampling area) may be examined utilizing µ-XRF.

6.2.3.3.2

Full-thickness float glass samples should be mounted float side down. Thinner fragments should be mounted to prevent elemental contribution from non-evidentiary sources (e.g. on X-ray permeable film (such as Kapton) using an adhesive that will not interfere with the sample spectra). For samples with

coatings (including float side) on both sides, the fractured surface (bulk glass) may be analyzed. Because the precision of μ-XRF is somewhat dependent on geometry and thickness, the questioned and known fragments should have similar thicknesses and a relatively flat surface at each sampling point.

6.2.3.3.3

Comparison of questioned and known glass via μ-XRF can be performed using spectral comparison and/or statistical evaluation of elemental ratios. Spectral comparison may consist of screening runs or detailed comparison runs. Spectral comparison consists of comparison of the elements present and their relative peak heights between questioned and known glass. Statistical evaluation of elemental ratios consists of comparisons of the ratios of the net intensity values of elements between questioned and known glass. Statistical evaluation may only be conducted on data from detailed comparison runs.

6.2.3.3.3.1 Spectral comparisons – screening

Screening comparisons may allow glass samples from different sources to be discriminated using short sampling durations based on differences in major elemental content. This may also allow for selection of appropriate fragments for detailed comparisons when many questioned fragments are present. A minimum of 3 replicates from the known glass and a minimum of 2 replicates from each questioned fragment should be collected.

Recommended parameters: Silicon Lithium detector (SiLi) instruments - at least 200 live sec; 50 kV; <50% Dead time. Silicon Drift detector (SDD) instruments – at least 120 live sec for single SDD, at least 60 live sec for double SDD; 50kV; <50% Dead time.

6.2.3.3.3.2 Spectral comparisons – detailed comparison runs

When practical, a minimum of 9 replicates from the known glass and a minimum of 3 replicates from each questioned fragment should be collected.

Recommended parameters: SiLi - at least 1200 liv sec; 50 kV; <50% Dead time. SDD – at least 600 for single SDD, at least 300 for double SDD; 50kV, <50% Dead time.

For exclusion: Observable differences in elemental spectra (different elements and/or readily apparent differences in relative peak heights).

For inclusion: No observable differences in elemental spectra. Statistical evaluation of elemental ratios should normally be conducted in this situation.

6.2.3.3.3.3 Statistical evaluation of elemental ratios

Any minor or trace element may be used in a ratio if it is quantifiable (SNR of 10 or more) in the questioned and/or known sample. If an element is not quantifiable in both questioned and known

samples, that element should not be used for comparison of ratios. If an element is quantifiable (SNR 10 or more) in one set and not identified (SNR of less than 3) in the other set, this difference can be used to discriminate the glass sets. Possible ratios for evaluation include, but are not necessarily limited to, Ca/Fe, Sr/Zr, Ca/Ti, Ca/K, Na/Mg, Ti/Fe, Sr/Fe, and Zr/Fe.

The analyst has discretion to use statistical methods suitable for the casework samples. These methods may include but are not limited to comparison of the ranges of ratios or +/-3 standard deviations of the known ratio average to each questioned ratio average.

- For inclusion: The statistical data of each evaluated ratio should be similar between questioned and known glass.
- For exclusion: The statistical data of at least one of the evaluated elemental ratios differ between the questioned and known glass.
- An analyst has discretion to report an inconclusive result with respect to µ-XRF in situations including, but not limited to: a glass sample does not give consistent data within a fragment; a fragment does not have a relatively flat sampling surface; a fragment is very small or very thin; or contamination of glass is suspected.

6.2.3.3.4 Quality assurance checks

Note: Also see TRACE-PM 7.5 Bruker M4 Tornado Micro-X-ray Fluorescence Spectrometry

Each day the XRF is used for casework analysis, it must pass quality control checks. For all XRF casework, these include calibration and a source performance check. For glass casework, additional checks include a system performance check and a scatter spectra check. For glass casework involving fragments <1mm in x and y dimensions, an X-ray spot check is also required.

6.2.3.3.4.1 Calibration

Within the calibration function of the instrument's software, set the parameters to 50 kV, 200 µA, 130000 cps, 40 keV, Zr, and K-a. Test the current calibration of each detector. If the displayed deviation from the current calibration is +/- 5eV, it is suitably calibrated. If the deviation for either detector is > +/- 5eV, calibrate each detector. After calibration, test the calibration of each detector. If deviations are +/- 5eV, it is suitably calibrated. Note the calibration results (pass/no-pass) in the case record.

6.2.3.3.4.2 Source/detector performance check

Using voltage and power settings of 50 kV and 300 µA, check the performance of the X-ray source and detectors using a known element standard (e.g., Cu). Record the cps values observed for each detector on a file on the instrument computer. Counts should not show appreciable drift (10% tolerance from prior reading). If the reading of either detector is <75% of prior readings, do not use that detector for casework. Note the source performance check results (pass/no-pass) in the case record.

6.2.3.3.4.3 System performance check

Using parameters of 50kV, 600 µA, and 300 live sec (double SDD) or 600 live sec (single SDD), collect a spectrum of NIST SRM 1831 (float glass). Save the spectrum on the instrument computer and print the spectrum (paper or electronic) with the Fe-Ka peak at ~50% of the display for retention in the case record.

6.2.3.3.4.4 Scatter spectra check

Using parameters of 50 kV, 200 µA, and 60 live sec, collect a scatter spectrum with each detector from the acrylic stage at x:2.3, y:1.3. Save spectra to the instrument computer. The check passes if the scatter spectra factors in 10-25 keV range are within 0.9-1.1 of the original scatter spectra. Note scatter spectra check results (pass/no-pass) in case record.

6.2.3.3.4.5 X-ray spot / camera alignment check

Using 'X Ray' circle of thick blue block of standards (provided by Bruker), verify that the X-ray spot is aligned with the 10x camera and 100x camera. For 10x, the fluorescence should be within the length of the cross-hairs. For 100x, the collection spot circle should be within the brighter fluorescence region. Note X-ray spot check results (pass/no-pass) in case record.

6.2.3.3.4.6 Bracket samples

If quantitative or semi-quantitative statistics will be evaluated, a reference sample should be analyzed at the beginning and end of casework sample data collection to verify the stability of the instrument throughout the data collection and to allow for inter-day comparison of data. To allow for comparison of data from different runs/days, reference sample spectra for those days should demonstrate consistency (spectral comparison method) and the parameters should be similar. This sample may be NIST SRM 1831 and can also function as the system performance check.

6.2.3.3.4.7 Control samples

A control sample should be collected to assess the possibility of elemental contribution from other sources (mounting medium, substrate, etc.). This may be done concurrent with casework samples or at a different time.

6.2.3.3.4.8 Technical review – data transfer/calculation check:

This check consists of targeted spot checks. One cell in each ratio column is checked to see that the elements correspond to the column header, one ratio range per graph is checked to make sure that they are pulling from the correct columns, and at least one ratio range per item/sample in the graphs is checked to make sure they are pulling from the correct rows.

6.2.3.3.5 End-use classification

End-use classification of questioned glass fragments may be possible based on relative ratios of certain elements. Published research should be consulted for this use.

6.2.4 General Guide for Examinations and Associations of Glass Evidence

XRF screening (<1200 live sec for SiLi; <600 for single SDD; <300 for double SDD):

- obvious elemental spectral differences: Elimination
- similar elemental spectra: Level 5 – Inconclusive Association (limited analysis performed for stronger conclusion to be reached)

XRF analysis (≥1200 live sec for SiLi; ≥600 for single SDD; ≥300 for double SDD):

- obvious elemental spectral differences: Elimination
- possible spectral differences and considerable unexplained differences in ratios: Elimination
- similar elemental spectra, slightly different in at least one element ratio: Level 5 – Inconclusive Association (minor variation due to several possible factors, particularly for thin fragments)
- similar elemental spectra, similar element ratios: Level 4 – Limited Association (limited analysis performed for stronger conclusion to be reached)

GRIM analysis:

- excluded by RI differences: Elimination
- inconclusive results by RI comparison: Level 5 - Inconclusive Association (limited analysis performed for stronger conclusion to be reached
- similar RI: Level 4 – Limited Association (limited analysis performed for stronger conclusion to be reached)

XRF analysis and GRIM analysis:

- excluded by spectral or RI differences: Elimination
- similar elemental spectra, slightly different in at least one element ratio, inconclusive RI: Inconclusive Non-association
- similar elemental spectra, slightly different in at least one element ratio; similar RI: Level 5 – Inconclusive Association (minor variation due to several possible factors, particularly for thin fragments)
- similar elemental spectra and ratios; inconclusive or similar RI: Level 3 – Association

Other factors may increase the significance and/or level of association, including but not limited to thickness of samples, comparison of coatings, surface texture, unusual elements or RI.

In general, an Item that has at least one fragment with a Level 3 Association to the known glass allows for additional analysis to stop for other fragments within that Item. However, based on circumstance of the case and the evidence, additional testing may be performed on the other fragments.

When the strongest association level within an item does not reach Level 3, additional examinations are typically warranted, which may include additional sampling of particles already analyzed or of other particles within the Item.

6.2.5 Determination of Direction of Impact Force for Glass Breakage

6.2.5.1

Attempt to piece the window back together and determine the approximate center point of the break.

6.2.5.2

Examine the rib markings (ridges) found on the edges of radial fractures of a number of broken pieces. See Diagram 1.

6.2.5.3

The rib markings (ridges) should be perpendicular to one edge of the glass and curve to become asymptotic (almost parallel) to the opposite ledge. Look for these markings.

6.2.5.4

The edge where the perpendicular is found is where the break in the glass occurred BUT the force/impact which broke the glass came from the opposite side (asymptotic side).

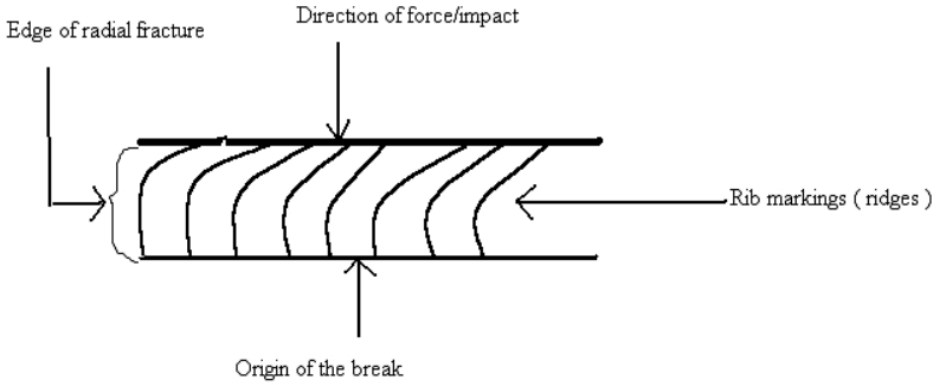


Diagram 1

6.2.5.5

The rib markings (ridges) will curve toward the center of the break- the point where the +impact occurred and where the radial fractures originate from.

6.2.5.6

Hackle markings may be observed along edges opposite to the perpendicular edge of the rib markings (ridges). These may occur when particularly high stress on the glass is placed.

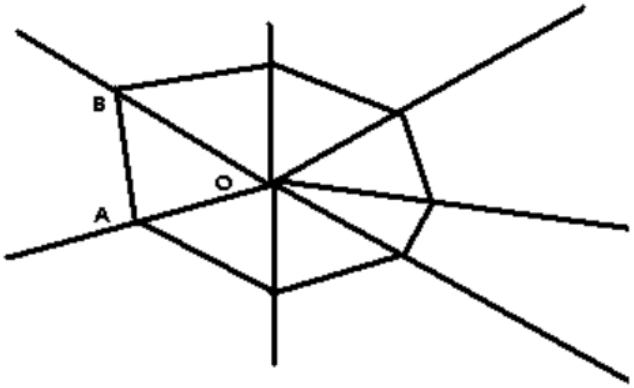
6.2.5.7

Rib markings (ridges) found on concentric fractures within first concentric circle will be the opposite to those found on the radial fractures.

6.2.6 Type of Fracture

6.2.6.1

OA: Radial Fracture (see diagram below)

6.2.6.2

AB: Concentric Fracture (see diagram below)