



# Standard Test Method for Forensic Comparison of Glass Using Micro X-ray Fluorescence ( $\mu$ -XRF) Spectrometry<sup>1</sup>

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## INTRODUCTION

One objective of a forensic glass examination is to compare glass specimens to determine if they can be discriminated using their physical, optical or chemical properties (for example, color, refractive index (RI), density, elemental composition). If the specimens are distinguishable, except for acceptable and explainable variations, in any of these observed and measured properties, it may be concluded that they did not originate from the same source of broken glass. If the specimens are indistinguishable in all of these observed and measured properties, the possibility that they originated from the same source of glass cannot be eliminated. The use of an elemental analysis method such as micro X-ray fluorescence spectrometry ( $\mu$ -XRF) yields high discrimination among sources of glass.

## 1. Scope

1.1 This test method is for the determination of major, minor, and trace elements present in glass fragments. The elemental composition of a glass fragment can be measured through the use of  $\mu$ -XRF analysis for comparisons of glass.

1.2 This test method covers the application of  $\mu$ -XRF using mono- and poly- capillary optics, and an energy dispersive X-ray detector (EDS).

1.3 This test method does not replace knowledge, skill, ability, experience, education, or training and should be used in conjunction with professional judgment.

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E2330 Test Method for Determination of Concentrations of Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Forensic Comparisons

## 3. Summary of Test Method

3.1  $\mu$ -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.

3.2 Glass fragments usually do not require sample preparation prior to analysis by  $\mu$ -XRF. Cleaning of specimens may be performed to remove any surface debris.

3.3 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.

3.4 Qualitative analysis is accomplished by identifying elements present in the specimen based on their characteristic X-ray energies.

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

3.5 Semi-quantitative analysis is accomplished by comparing the relative area under the peaks of characteristic X-rays of certain elements.

3.6 Spectral and elemental ratio comparisons of the glass specimens are conducted for source discrimination or association.

#### 4. Significance and Use

4.1  $\mu$ -XRF provides a means of simultaneously detecting major, minor, and trace elemental constituents in small glass fragments such as those frequently examined in forensic case work. It can be used at any point in the analytical scheme without concern for changing sample shape or sample properties, such as RI, due to its totally nondestructive nature.

4.2 Limits of detection (LOD) are dependent on several factors, including instrument configuration and operating parameters, sample thickness, and atomic number of the individual elements. Typical LODs range from parts per million ( $\mu\text{g g}^{-1}$ ) to percent (%).

4.3  $\mu$ -XRF provides simultaneous qualitative analysis for elements having an atomic number of eleven or greater. This multi-element capability permits detection of elements typically present in glass such as magnesium (Mg), silicon (Si), aluminum (Al), calcium (Ca), potassium (K), iron (Fe), titanium (Ti), strontium (Sr), and zirconium (Zr), as well as other elements that may be detectable in some glass by  $\mu$ -XRF (for example, molybdenum (Mo), selenium (Se), or erbium (Er)) without the need for a predetermined elemental menu.

4.4  $\mu$ -XRF comparison of glass fragments provides additional discrimination power beyond that of RI or density comparisons, or both, alone.

4.5 The method precision should be established in each laboratory for the specific conditions and instrumentation in that laboratory.

4.6 When using small fragments having varying surface geometries and thicknesses, precision deteriorates due to take-off-angle and critical depth effects. Flat fragments with thickness greater than 1.5 mm do not suffer from these constraints, but are not always available as questioned specimens received in casework. As a consequence of the deterioration in precision for small fragments and the lack of appropriate calibration standards, quantitative analysis by  $\mu$ -XRF is not typically used.

4.7 Appropriate sampling techniques should be used to account for natural heterogeneity of the material, varying surface geometries, and potential critical depth effects.

4.8 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may also be used for trace elemental analysis of glass and offer lower minimum detection levels and the ability for quantitative analysis. However, these methods are destructive, and require larger sample sizes and much longer sample preparation times (Test Method **E2330**).

4.9 Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) uses comparable specimen sizes to those used for  $\mu$ -XRF but offers better LODs, quantitative

capability and less analysis time. LA-ICP-MS drawbacks are greater instrument cost and complexity of operation.

4.10 Scanning Electron Microscopy with EDS (SEM-EDS) is also available for elemental analysis, but it is of limited use for forensic glass source discrimination due to poor detection limits for higher atomic number elements present in glass at trace concentration levels. However, discrimination of sources that have indistinguishable RIs and densities may be possible.

#### 5. Interferences

5.1 Peak overlaps occur in various regions of the EDS spectrum (**1**).<sup>3</sup> In glass, such interferences include the overlap of characteristic X-ray lines (for example, Ti K-series and Ba L-series), sum peaks, primary X-ray source excitation peaks (for example, Rh), and escape peaks. In general, automated deconvolution algorithms are included in data processing software that adequately address such overlaps. EDS spectra shall be manually inspected to ensure that potential peak overlaps are considered and addressed.

#### 6. Apparatus

6.1 A  $\mu$ -XRF spectrometer with an EDS detector is employed. Most commercial-grade  $\mu$ -XRF systems with EDS detectors should be adequate for forensic analysis of glass. The  $\mu$ -XRF system must, however, meet the following performance specifications:

6.1.1 The spot size(s) must be within the range(s) of approximately 10  $\mu\text{m}$  to 2 mm; the spot size used may be adjustable to different sizing for instruments with appropriate optics.

6.1.2 The instrument must be capable of operating at an accelerating voltage of 35 kV or greater.

6.1.3 The EDS detector must be capable of a resolution that is typically less than 180 eV, measured as the full width at half the maximum height of the Mn  $K\alpha$  peak; better resolutions will provide improved discrimination of adjacent or overlapping peaks, or both.

6.1.4 A calibrated, scaled display of energy units (keV) and the ability to identify and label X-ray lines is required for the EDS system.

6.2 *Energy Calibration Material*—Capable of calibrating the EDS detector at both the low (<2 keV) and high (>6 keV) X-ray spectral regions.

6.3 An X-ray source that does not yield significant spectral interferences with the characteristic X-ray lines for the elements typically found in glass is required. Several X-ray sources are available; a rhodium X-ray source is preferred for appropriate excitation energy and minimal spectral interferences for elements in glass. Other X-ray sources such as Mo X-ray tubes cause interferences with discriminating elements such as Zr.

6.4 A vacuum sample chamber, sample stage, and visualization system are required.

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

6.5 The sample holder, sample support film, and mounting material (for example, adhesive with low trace elements) must prevent background interferences.

## 7. Hazards

7.1 The X-ray sources emit radiation when energized. For operator safety, appropriate shielding and safety interlocks must be in place and operational.

## 8. Calibration and Standardization

8.1 *Apparatus*—The instrument must be optimized as in accordance with manufacturer's instruction.

8.1.1 *Energy Calibration*—Calibrate the X-ray energy scale to characteristic X-ray emission lines by either measuring the centroid energy of a low- (<2 keV) and high- (>6 keV) energy peak or by using software provided by the instrument manufacturer. For example, the aluminum (1.486 keV) and copper (Cu) (8.040 keV)  $K\alpha$ -X-ray energy lines may be used.

8.1.2 *Stage Calibration*—For automated or multiple point analysis, initialize the stage position to assure that the stage coordinates accurately reflect the stage position.

### 8.1.3 *Optical Alignment:*

8.1.3.1 Align X-ray optics to obtain the maximum count rate.

8.1.3.2 Align visualization optics to ensure that the visual target area coincides with the X-ray beam position.

8.1.4 *Spot Size Measurement*—Determine spot size of the X-ray beam at the focal point of the visualization optics. For instruments with continuous variable spot size options, determine the spot size at multiple settings and interpolate the others.

8.1.5 *Reference Materials*—Analyze a glass certified reference material (CRM) (for example, NIST SRM 1831) to verify the calibration of X-ray energy lines for elements present in glass and determine if the instrument response is within acceptable limits. Measure this glass CRM using the same analysis parameters as the glass specimens. Use this reference glass sample to normalize element ratios for interlaboratory comparisons, intralaboratory data collection from different analytical runs, and databasing applications to improve precision.

8.1.6 *Blanks*—Collect a spectrum of a specimen devoid of elements having an atomic number of 11 or greater, such as the plastic stage plate or an area of the support material having no glass present. Record any system peaks present for future reference.

### 8.2 *Quality Assurance:*

8.2.1 The performance of the instrument must be monitored routinely and the frequency and tolerances should be set by each laboratory.

8.2.1.1 Check the system calibration prior to the performance of an analysis.

8.2.1.2 Check the performance of the X-ray source using a known element standard (for example, Cu). Maximum counts for the system should be obtained utilizing system operating parameters established by the laboratory. Maximum counts should not show appreciable drift from acceptable parameters

established by the laboratory or analyst for this procedure (10 % tolerance is recommended).

8.2.2 Demonstrate that Ti and Sr have LOD in a soda-lime glass matrix of 75 ppm or less (as described in 11.1) for the instrumental parameters used for collection of spectra from the glass specimens. NIST SRM 1831 is a suitable sample for this purpose.

## 9. Procedure

### 9.1 *Specimen Preparation:*

9.1.1 Examine glass fragments using stereomicroscopy to determine an appropriate preparation method for the specimen.

9.1.2 If necessary, clean the specimen to remove any surface contamination. Cleaning may include washing specimens with soap and water, with or without ultrasonication, and rinsing in deionized water, followed by rinsing in acetone, methanol, or ethanol, and drying. Soaking in various concentrations of nitric acid for 30 minutes or longer, rinsing with deionized water and ethanol, and drying prior to analysis removes most surface contamination without affecting the measured concentrations of elements inherent in the glass. However, the use of nitric acid may remove any surface coating that may be present.

### 9.1.3 Mount the specimen for analysis.

9.1.3.1 The specimen mounting technique depends on the sample size and shape, beam size, X-ray fluorescence spectrometer chamber design and purpose of the examination.

9.1.3.2 Raise specimens off the surface of the stage for analysis using an X-ray transparent sample holder or supportive X-ray film, or both. This positioning reduces X-ray scatter off of the surface of the stage and, hence, improves sample signal-to-noise. Because analysis is performed under vacuum, ensure that specimens retain their position on the sample holder by securing with adhesive. Prior to analysis, analyze a small amount of the adhesive to determine the presence of any elements that could interfere with those in the specimen. When small amounts of adhesive are used and beam overspill (X-ray beam extending beyond the perimeter of the specimen) is avoided, little to no interference from the adhesive will be observed.

9.1.3.3 Position specimens to present as flat a surface as possible to the impinging excitation X-ray beam. If necessary, use a small amount of adhesive to facilitate this positioning.

9.1.3.4 For comparisons, glass specimen should be of similar size, shape, and thickness to each other. For full thickness fragments of float glass, comparisons should be made between similar surface types (for example, non-float surface to non-float surface).

9.1.4 Place sample(s) in the instrument's analysis chamber. For automated multiple point analyses, it may be necessary to secure the sample/sample holder to the instrument stage.

9.1.5 Evacuate the chamber; samples should be run under vacuum.

9.1.6 Target specimen areas that are relatively flat in topography and focus imaging optics. Avoid excitation beam overspill when possible.

9.2 *Operating Conditions*—The following are suggested as a general guide for instrument operating conditions:



9.2.1 Turn on the X-ray source. Set the excitation voltage to at least 35 kV in order to provide sufficient overvoltage necessary for efficient X-ray excitation of the K-lines of higher atomic number elements, such as As, Rb, Sr, Zr, and Mo. Higher beam energies will typically improve detection limits of those elements. Once the beam excitation voltage is established, it should not be changed between specimens in a given comparison set. Most of the X-ray lines produced may be displayed with an energy range of 0 to 20 keV.

9.2.2 Select an appropriate X-ray optic size for the analysis of the specimen. For instruments with variable spot size options, this size is determined from the setpoint calibrated as described in 8.1.4. Once the spot size is established, it should not be changed between specimens in a given comparison set.

9.2.3 Set the pulse processor time constant at a midrange value; this is a compromise between maximum count rate and maximum spectral resolution. The optimal count rate is generally provided by the instrument manufacturer. Once established, do not change the pulse processor time between specimens in a given comparison set.

9.2.4 Adjust the beam current for each specimen as needed to yield a maximum X-ray detector dead time not to exceed 50 percent.

### 9.3 Specimen Analysis:

9.3.1 For each specimen, collect a spectrum for a live time that provides reasonable counting statistics for trace element peaks. For a  $\mu$ -XRF system with a 100  $\mu$ m monocrapillary and a Si(Li) detector, 1200 live seconds is generally sufficient.

9.3.2 Collect replicate spectra to ensure that the questioned glass fragments and known glass source(s) are adequately characterized. When practical, analyze a minimum of three replicates on each questioned specimen examined and nine replicates on known glass sources.

## 10. Calculation and Interpretation of Results

10.1 Examine the spectrum, and identify and label the peaks.

10.2 Characteristic X-ray energies may be obtained from automatic element identification software; however, peak identifications shall be manually verified. Energy slide rules, computer generated theoretical fit curves that can be superimposed on the spectrum, and published tables can be used for this purpose.

10.3 Spectral artifacts, such as sum peaks and escape peaks associated with the major peaks, should be considered and corrected.

10.4 In addition to the higher energy peaks, verify the presence of any lower energy peaks and their expected relative intensities. Individual asymmetric peaks and inconsistent peak ratios within a family may indicate a peak overlap.

10.5 When the area of a characteristic energy of an element has a signal-to-noise ratio of three or more, that element may be identified. This criterion may not apply when spectral artifacts, overlapping energies of other elements, or shoulder peaks, or a combination thereof, are present within the characteristic energy range of that element.

10.6 Compare the spectra using peak identification, spectral comparisons, and peak intensity ratio comparisons.

10.6.1 *Peak Identification*—Compare detected elements of the questioned and known glass spectra.

10.6.2 *Spectral Comparisons*—Visually compare the spectral shapes and relative peak heights of the questioned and known glass specimen spectra.

10.6.3 *Peak Intensity Ratio Comparisons*—When the area of a characteristic energy peak of an element has a signal-to-noise ratio of ten or more, that element may be used in semi-quantitative analysis such as peak intensity ratio comparisons. This criterion may not apply when spectral artifacts, overlapping energies of other elements, or shoulder peaks, or a combination thereof, are present within the characteristic energy range of that element. Evaluate elemental peak intensity ratios of the questioned and known glass spectra. Ratios for evaluation can include: Ca/Mg, Ca/Ti, Ca/Fe, Sr/Zr, Fe/Zr, and Ca/K, if those elements are present above the limit of quantitation (LOQ). These peak intensity ratio comparisons have been shown to provide the best discrimination among different sources of soda-lime glasses. Additional ratios should be chosen based on the elements present in the specimens. Improved precision may be obtained using ratios of peak intensities of elements close in atomic number because the effects of take-off angle are reduced. The elements present in the numerator and denominator of the ratio can be inverted if the denominator is a small number. Caution should be exercised when accepting background fits generated by automatic peak integration software because automatic background corrections are prone to errors. Therefore, manual adjustment of the background is recommended.

### 10.7 Interpretation of Comparisons:

10.7.1 *Peak Identification*—Reproducible differences in detected elements between specimens demonstrate that the specimens have different sources. When peak identification does not discriminate between the specimens, further spectral comparisons should be conducted.

10.7.2 *Spectral Comparisons*—Reproducible differences in spectral shapes and relative peak heights between specimens may indicate that the specimens have different sources. Peak intensity ratios can be calculated to demonstrate this difference. When evaluation of spectral shapes and relative peak heights do not discriminate between the specimens, peak intensity ratios should be calculated.

10.7.3 *Peak Intensity Ratio Comparisons*—Reproducible differences between specimens in peak intensity ratios can demonstrate that the specimens have different sources. One of the two following statistical measures is recommended to assess the association or discrimination of the samples based on elemental ratios (2-6):

10.7.3.1 *Elemental Ratio Range Overlap*—For each elemental ratio, compare the range of the questioned specimen replicates to the range for the known specimen replicates (3, 4). Because standard deviations are not calculated, this statistical measure does not directly address the confidence level of an association. If the ranges of one or more elements in the questioned and known specimens do not overlap, it may be concluded that the specimens are not from the same source.