



Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons¹

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INTRODUCTION

One objective of a forensic glass examination is to compare glass samples to determine if they can be discriminated by their physical, optical, or chemical properties (for example, color, refractive index (RI), density, elemental composition). If the samples are distinguishable in any of these observed and measured properties, it can be determined that they did not originate from the same source of broken glass. If the samples are indistinguishable in all these observed and measured properties, the possibility exists that they originated from the same source of glass. The use of an elemental analysis method such as laser ablation inductively coupled plasma mass spectrometry yields high discrimination among sources of glass.

1. Scope

1.1 This test method covers a procedure for the quantitative elemental analysis of the following seventeen elements: lithium (Li), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), iron (Fe), titanium (Ti), manganese (Mn), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba), lanthanum (La), cerium (Ce), neodymium (Nd), hafnium (Hf) and lead (Pb) through the use of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the forensic comparison of glass fragments. The potential of these elements to provide the best discrimination among different sources of soda-lime glasses has been published elsewhere (1-5).² Silicon (Si) is also monitored for use as a normalization standard. Additional elements may be added as needed, for example, tin (Sn) can be used to monitor the orientation of float glass fragments.

1.2 The method only consumes approximately 0.4 μg to 3 μg of glass per replicate and is suitable for the analysis of full thickness samples as well as irregularly shaped fragments as

small as 0.1 mm by 0.1 mm by 0.2 mm (6) in dimension. The concentrations of the elements listed above range from the low parts per million ($\mu\text{g}\text{g}^{-1}$) to percent (%) levels in soda-lime glass, the most common type encountered in forensic cases. This standard method can be applied for the quantitative analysis of other glass types; however, some modifications in the reference standard glasses and the element menu may be required.

1.3 This standard is intended for use by competent forensic science practitioners with the requisite formal education, discipline-specific training (see Practice E2917), and demonstrated proficiency to perform forensic casework.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This test method is under the jurisdiction of ASTM Committee E30 on Forensic Sciences and is the direct responsibility of Subcommittee E30.01 on Criminalistics.

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² The boldface numbers in parentheses refer to a list of references at the end of this standard.

2. Referenced Documents

2.1 *ASTM Standards*:³

C162 Terminology of Glass and Glass Products

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

E2917 Practice for Forensic Science Practitioner Training, Continuing Education, and Professional Development Programs

E2926 Test Method for Forensic Comparison of Glass Using Micro X-ray Fluorescence (μ -XRF) Spectrometry

3. Terminology

3.1 *Definitions*:

3.1.1 *calibration standard, n*—a reference material used to determine the concentrations of the analyte elements in the glass matrix. The calibration standard(s) shall have a known elemental composition including a known uncertainty for the reported analytes.

3.1.2 *glass, n*—an inorganic product of fusion that has been cooled to a rigid condition without crystallization. **C162**

3.1.3 *normalization standard, n*—an element that is present in the glass matrix at elevated and relatively homogeneous concentration that may be used to normalize the laser ablation signal to compensate for any variation on the ablated mass or instrumental drift.

4. Summary of Test Method

4.1 The glass fragments usually do not require sample preparation prior to the LA-ICP-MS analysis. However, they can be washed with solvents or pre-ablated if necessary.

4.2 The glass fragment is placed inside an ablation chamber and a laser beam is focused on the surface of the sample. When the ablation is started, the interaction between the pulsed laser and the sample surface produces a cloud of very small particles, which are transported from the ablation cell by a carrier gas into the ICP-MS for analysis.

4.3 An ICP-MS is used to quantify the elements of interest.

4.4 Quantitative analysis is accomplished using well-characterized glass standards whose major elemental composition is similar to the material to be analyzed.

4.5 A comparison between the reported elemental compositions of the known and questioned glass fragments may result in a decision on whether the samples are distinguishable or indistinguishable by elemental composition.

5. Significance and Use

5.1 This test method is useful for the determination of elemental concentrations in the range of approximately

$0.1 \mu\text{g g}^{-1}$ to 10 percent (%) (See Table X1.1) in soda-lime glass samples (**7** and **8**). A standard test method can aid in the interchange of data between laboratories and in the creation and use of glass databases.

5.2 The determination of elemental concentrations in glass provides high discriminating value in the forensic comparison of glass fragments.

5.3 This test method produces minimal destruction of the sample. Microscopic craters of $50 \mu\text{m}$ to $100 \mu\text{m}$ in diameter by $80 \mu\text{m}$ to $150 \mu\text{m}$ deep are left in the glass fragment after analysis. The mass removed per replicate is approximately $0.4 \mu\text{g}$ to $3 \mu\text{g}$ (**6**).

5.4 Appropriate sampling techniques shall be used to account for natural heterogeneity of the materials at a microscopic scale.

5.5 The precision, bias, and limits of detection of the method (for each element measured) shall be established during validation of the method. The measurement uncertainty of any concentration value used for a comparison shall be recorded with the concentration.

5.6 Acid digestion of glass followed by either Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) can also be used for trace elemental analysis of glass, and offer similar detection levels and the ability for quantitative analysis. However, these methods are destructive, and require larger sample sizes and more sample preparation (Test Method **E2330**).

5.7 Micro X-Ray Fluorescence (μ -XRF) uses comparable sample sizes to those used for LA-ICP-MS with the advantage of being non-destructive of the sample. Some of the drawbacks of μ -XRF include lower sensitivity and precision, and longer analysis time (Test Method **E2926**).

5.8 Scanning Electron Microscopy with Energy Dispersive Spectrometry (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, distinguishing between sources having similar RIs and densities is sometimes possible.

6. Apparatus

6.1 *LA-ICP-MS*—A Laser Ablation system coupled to an ICP-MS instrument is employed. Since there are several manufacturers for both laser ablation units and ICP-MS instruments, the instrument maker, model, configuration, and major operational parameters (that is, laser wavelength for the laser and mass selective detector type for the ICP-MS) of both instruments shall be noted within the analysis results. The most common laser wavelengths used for glass analysis are 266 nm, 213 nm, and 193 nm. Either quadrupole or magnetic sector ICP-MS instruments are suitable for this test method.

6.2 Prior to analysis, the ICP-MS shall be tuned according to the manufacturer's recommendations covering the mass range of the elements to be measured. Detector cross calibrations (pulse/analog) shall be performed when two detector

³ 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.

modes are used in the analysis. The instrument shall be adjusted for maximum sensitivity, best precision, and to minimize oxides and doubly charged ion interferences. The use of a glass reference material, such as NIST 612,⁴ is recommended during the tuning and performance check.

6.3 In order to prepare for data acquisition, the signals of the following isotopes are monitored in the ICP-MS; lithium (⁷Li), magnesium (²⁴ or ²⁵Mg), aluminum (²⁷Al), silicon (²⁹Si), potassium (³⁹K), calcium (⁴²Ca), iron (⁵⁷Fe), titanium (⁴⁹Ti), manganese (⁵⁵Mn), rubidium (⁸⁵Rb), strontium (⁸⁸Sr), zirconium (⁹⁰Zr), tin (¹¹⁸Sn), barium (¹³⁷Ba), lanthanum (¹³⁹La), cerium (¹⁴⁰Ce), neodymium (¹⁴⁶Nd), hafnium (¹⁸⁰Hf) and lead (²⁰⁸Pb). This procedure can be applicable to other elements and other isotopes (for example, ²⁰⁶, ²⁰⁷Pb); however, those elements listed above are considered to provide the most discrimination power for soda-lime glass comparisons. Alternatively, other isotopes such as ⁵⁶Fe may be monitored using ICP-MS with advanced technology to remove interferences (for example, sector field ICP-MS or reaction cells).

6.4 Helium is used as the carrier gas to transport the particles from the ablation cell to the plasma. The use of helium carrier gas has been reported to result in fewer fractionation effects than the use of argon as a carrier (9).

7. Hazards

7.1 Commercial laser ablation units are enclosed type I lasers. However, laser systems typically used for analysis of glass generate high energy radiation that can pose serious risks to eye safety if exposed to the eye. Interlocks shall not be bypassed or disconnected.

7.2 The argon plasma shall not be observed directly without protective eyewear. Potentially hazardous UV light can be emitted.

7.3 ICP-MS instruments generate high amounts of radiofrequency energy (RF) in their RF power supply and torch boxes that is potentially hazardous if allowed to escape. Safety devices and safety interlocks shall not be bypassed or disconnected.

8. Calibration and Standardization

8.1 A calibration curve using multiple glass standards or using a single glass standard is used for quantitation for LA-ICP-MS analysis of glass. Any calibration standard shall be matrix-matched to the sample and well-characterized. The calibration standard(s) shall be traceable to an accepted standard. For glass analysis there are several standards that are available. They include the NIST Standard Reference Materials NIST 610, NIST 612, and NIST 614; the float glass standard glasses FGS1 and FGS2, evaluated by the European group NITECRIME (5) and distributed by the Bundeskriminalamt, Germany;⁵ and the calibration standards CFGS1, CFGS2, and

CFGS3 evaluated by the NIJ Glass Interpretation Working Group and distributed by Florida International University, USA (8, 10).

8.2 In addition to the calibration standard, at least one additional glass standard reference material (that is, “calibration verification standard”) shall be measured with each sample set as a quality control check for the accuracy and precision of the method. The quality control specifications shall be set by each Forensic Science Service Provider (FSSP). The quality control check standard should be a well-characterized glass and one not used to calibrate the instrument.

8.3 As a minimum, calibration standards are required at the beginning and the end of the analytical sequence in order to adjust for instrument drift over time. Acceptance criteria for the calibration shall be defined by validation protocols and shall include the use of calibration verification standards.

8.4 A normalization standard, preferably silicon (²⁹Si), shall be used to normalize the signal. The use of a normalization standard is needed to adjust for differences in ablation yield between the ablated materials. Since silicon is present as a major component in all soda-lime glass (~70 % to 72 % as SiO₂) (3, 11), a low abundance isotope (²⁹Si) is commonly used as the normalization standard for this method.

9. Procedure

9.1 If necessary, clean the samples to remove any surface contamination by washing or pre-ablation, or both, prior to analysis.

NOTE 1—Cleaning can include washing samples in soap or water, ultrasonication, or additional rinses in deionized water then acetone, methanol, or ethanol, before drying. In addition, soaking in dilute concentrations of nitric acid for at least 30 minutes and rinsing in deionized water and ethanol removes most surface contamination without affecting the elemental concentrations of interest. However, nitric acid can unintentionally remove surface coatings on the sample.

9.2 Multiple samples and standards can be placed together in the ablation cell as long as their positions are documented.

9.3 Secure the samples or standards, or both, in the ablation cell using double-sided tape, other adhesive, or putty. Orient the sample to avoid an original surface of the glass. The following steps shall be followed:

9.3.1 After opening the ablation cell for sample exchange, purge the cell with the carrier gas to avoid any contamination.

9.3.2 If pre-ablation cleaning is performed, it can be done at this point.

9.3.3 Focus the laser beam at the surface of the sample. Spot sizes of ~50 μm to 100 μm and a repetition rate of 10 Hz are recommended.

9.3.4 Initiate the acquisition of the analytical signals using the ICP-MS software. Each data acquisition consists of a transient signal of intensity versus time for each element. Each transient signal shall include a background (gas blank) measurement (typically 20 s to 40 s), followed by the ablation of the sample (typically 30 s to 60 s). A washout delay (typically 30 s to 60 s) shall be applied between two measurements to avoid carryover.

NOTE 2—The background, ablation and washout delay intervals will

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

⁵ Available from Bundeskriminalamt, Section KI 42, 65173 Wiesbaden, Germany, <http://www.bka.de>.

vary depending upon instrumental configurations and the needs of the analysis. Specific intervals should be determined by validation procedures.

9.4 Conduct replicate ablations at different locations within the fragment(s). If the size allows, space the fragments sufficiently apart to avoid re-ablating possible debris from other ablation halos.

9.5 Collect replicate measurements to ensure that the questioned glass fragments and known glass source(s) are adequately characterized in all dimensions (7). Analyze a minimum of three replicates on each questioned sample examined and nine replicates on known glass sources.

9.5.1 If the size of the questioned samples allows, perform four to six measurements on each questioned sample.

9.5.2 If the number and size allow, analyze at least three replicate measurements on four different fragments of each known sample (that is, 12 replicate measurements total) for tempered glass sources, or at least nine replicate measurements spaced over separate areas of one adequately-sized fragment of a non-tempered source. For smaller fragments, the nine replicate measurements can be accomplished with more samples and fewer replicates per sample.

NOTE 3—If it is not possible to analyze the minimum recommended number of known replicates (see 9.5.2) the elemental heterogeneity may not be captured in the source. This could potentially increase the false exclusion rate.

9.6 Analyze at least one calibration standard at the beginning and the end of a sequence. Additional standards can be added.

9.7 Measure at least three replicates of one quality control standard (that is, calibration verification standard) within each sequence.

9.8 Longer sequences can be bracketed into sets of up to 40 ablation spots (that is, sequences) by adding additional triplicate measurements of the calibration standard(s).

NOTE 4—It is recommended that the entire sequence be completed in a single session (a single day). As an example, when four fragments of a single known sample are compared to two questioned fragments, the

analytical sequence can be as follows:

- (1) Calibration standard(s) (spots 1-3)
- (2) “Known” fragment #1 (spots 1-3)
- (3) “Questioned” fragment #1 (spots 1-3)
- (4) Quality Control Standard(s) (spots 1-3)
- (5) “Questioned” fragment #1 (spots 4-6)
- (6) “Known” fragment #2 (spots 4-6)
- (7) Calibration standard(s) (spots 4-6)
- (8) “Known” fragment #3 (spots 7-9)
- (9) “Questioned” fragment #2 (spots 1-3)
- (10) Quality Control Standard(s) (spots 4-6)
- (11) “Questioned” fragment #2 (spots 4-6)
- (12) “Known” fragment #4 (spots 10-12)
- (13) Calibration standard(s) (spots 7-9)

NOTE 5—A symmetrical arrangement of the analytical sequence of standards and samples is advantageous in minimizing the effects that may result from instrumental drift.

9.9 Once the acquisition is completed, use the software of choice to integrate the transient signals and determine the element concentrations of the samples. Some data reduction software allows real time data reduction so the analytical data can be immediately checked after each ablation.

9.10 For each isotope, the transient signal shall be integrated, corrected for the gas blank and normalized to the ²⁹Si normalization standard signal. Convert the normalized signals to element concentration units using the calibration. The data reduction software used is selected by each FSSP. Due to particle size effects that may lead to undesired fractionation, it is recommended that the unstable signal collected during the beginning of the ablation not be integrated. See Fig. 1 for illustration of transient signal integration recommendation.

NOTE 6—When an anomaly is suspected in the transient signal, it is recommended that an outlier test be conducted. If a data point is rejected, the reason for the rejection shall be documented in the technical record.

10. Limits of detection (LOD) and Limit of Quantitation (LOQ)

10.1 Limits of detection and limits of quantitation were determined by laboratory analysis procedures prior to publication of this test method. Limits of detection (LOD) were

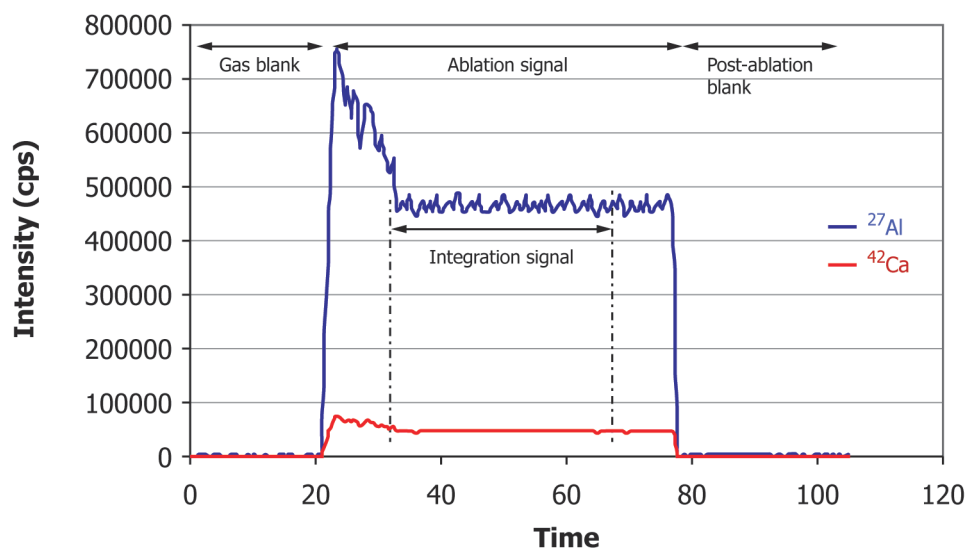


FIG. 1 Example Ablation Signal for Glass