



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 using 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 may be concluded that they did not originate from the same source of broken glass. If the samples 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 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 an internal standard. Additional elements can 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 to 2 g 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 0.4 mm in dimension. The concentrations of the elements listed above range from the low parts per million ($\mu\text{g g}^{-1}$) to percent (%) levels in soda-lime-silicate glass, the most common type encountered in forensic cases. This

standard method may 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 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*:³

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

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

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.

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.

3. Summary of Test Method

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

3.2 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.

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

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

4. Significance and Use

4.1 This test method is useful for the determination of elemental concentrations in the microgram per gram ($\mu\text{g g}^{-1}$) to percent (%) levels in soda-lime glass samples. A standard test method can aid in the interchange of data between laboratories and in the creation and use of glass databases.

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

4.3 This test method produces minimal destruction of the sample. Microscopic craters of 50 to 100 μm in diameter by 80 to 150- μm deep are left in the glass fragment after analysis. The mass removed per replicate is approximately 0.4 to 3.1 μg .

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

4.5 The precision, accuracy, and limits of detection of the method (for each element measured) should be established in each laboratory that employs the method. The measurement uncertainty of any concentration value used for a comparison should be recorded with the concentration.

4.6 Acid digestion of glass followed by either Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may 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 much longer sample preparation times (Test Method E2330).

4.7 Micro X-Ray Fluorescence ($\mu\text{-XRF}$) 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 $\mu\text{-XRF}$ are poorer sensitivity and precision, and longer analysis time.

4.8 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, distinguishing between sources having similar RIs and densities is possible.

5. Apparatus

5.1 *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 should 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.

5.2 Prior to the analysis on the day it is used, the ICP-MS should be tuned according to the manufacturer's recommendations covering the mass range of the elements to be measured. The instrument should be adjusted for maximum sensitivity, best precision, and to minimize oxides and doubly charged ion interferences. The use of a well-characterized glass standard, such as NIST 612,⁴ is recommended during the tuning and performance check. Detector cross calibrations (pulse/analog) should be performed before any measurements when two detector modes are used in the analysis.

5.3 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 may 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 can be monitored using ICP-MS with advanced technology to remove interferences (for example, sector field ICP-MS or reaction cells).

5.4 Either argon or helium can be used as a 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 (6).

6. Hazards

6.1 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 should not be bypassed or disconnected.

6.2 The argon plasma should not be observed directly without protective eyewear. Potentially hazardous UV light may be emitted.

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

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

7. Calibration and Standardization

7.1 A calibration curve using multiple glass standards or using a single glass standard can be used for quantitation for LA-ICP-MS analysis of glass. Any standard used to create the calibration should be matrix-matched to the sample and well-characterized. The calibration standard(s) must be traceable to an accepted standard. For glass analysis there are several standards that are available such as the NIST Standard Reference Materials (that is, NIST 610, NIST 612, NIST 614) and the float glass standard glasses (FGS1, FGS2) evaluated by the European group NITECRIME (5) and distributed by the Bundeskriminalamt, Germany.⁵ An internal standard, preferably silicon (²⁹Si), must be used to normalize the signal. The use of an internal 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), a low abundance isotope (²⁹Si) is commonly used as the internal standard for this method. If this method is used for the analysis of other glass types, the concentration of the internal standard must be determined prior to quantitative analysis.

7.2 In addition to the calibration standard, at least one glass verification standard should be measured with each sample set as a quality control check for the accuracy and precision of the method. The quality control specifications should be set by each laboratory.

7.3 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 must be defined by each laboratory and should include the use of calibration verification standards.

8. Procedure

8.1 If necessary, samples may be cleaned to remove any surface contamination by washing or pre-ablation, or both, prior to analysis. Cleaning may include washing samples 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 some surface coatings that may be present.

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

8.3 The samples or standards, or both, must be secured in the ablation cell using double-sided tape or other adhesive. Orient the sample to avoid an original surface of the glass. The known and questioned samples should be treated equally.

8.4 Purge the ablation cell with the carrier gas between samples to avoid any contamination.

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

8.6 Focus the laser beam at the surface of the sample. Single spot (or depth profile) ablation modes are recommended at a spot size of ~50 to 100 μm and a repetition rate of 10 Hz. Program the laser parameters.

8.7 Initiate the acquisition of the analytical signals using the ICP-MS software. Each data acquisition will be comprised of a transient signal of intensity versus time for each element; each transient will include 20-30 seconds of background (gas blank) measurement, followed by 50-60 seconds of ablation of the sample, followed by 10-30 seconds of post-ablation blank measurement.

8.8 Conduct replicate ablations at different locations within the fragment(s). Locations should be spaced sufficiently to avoid possible debris from other ablation halos. Collect replicate measurements to ensure that the questioned glass fragments and known glass source(s) are adequately characterized. Analyze a minimum of three replicates on each questioned sample examined and nine replicates on known glass sources.

8.9 It is recommended that the entire sequence be completed in a single session (a single day). As an example, when a known sample with 3 fragments is compared to a single recovered fragment, the analytical sequence may be as follows:

(1)	Calibration standard	(1 st , 2 nd , and 3 rd spot)
(2)	"Known" fragment #1	(1 st , 2 nd , and 3 rd spot)
(3)	"Recovered" fragment	(1 st , 2 nd , and 3 rd spot)
(4)	Calibration verification standard	(1 st , 2 nd , and 3 rd spot)
(5)	"Known" fragment #2	(1 st , 2 nd , and 3 rd spot)
(6)	"Known" fragment #3	(1 st , 2 nd , and 3 rd spot)
(7)	Calibration standard	(4 th , 5 th , and 6 th spot)

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

8.10 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.

8.11 For each isotope, the transient signal is integrated, corrected for the gas blank and normalized to the ²⁹Si internal standard signal. The normalized signals are converted to element concentration units using the calibration. The data reduction software is selected by each laboratory. Because of particle size effects that may lead to undesired fractionation, it is recommended that the first 15 seconds or more of data collected during ablation not be integrated. See Fig. 1 for illustration of transient signal integration recommendation.

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

9.1 Limits of detection (LOD) were determined for each element by measuring procedure blanks on two non-consecutive days using a quadrupole ICP-MS and a Nd-YAG 213-nm laser. Each day, the mean and standard deviation of replicate measurements were calculated. LODs were computed as 3 times the standard deviation. LOQs were computed as 10

⁵ Available from Bundeskriminalamt, Section KI 35, 65173 Wiesbaden, Germany, <http://www.bka.de>.