



Standard Test Method for Determination of Concentrations of Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Forensic Comparisons¹

This standard is issued under the fixed designation E2330; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 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 inductively coupled plasma mass spectrometry yields high discrimination among sources of glass. **(1-16)**²

1.2 This test method covers a procedure for quantitative determination of the concentrations of magnesium (Mg), aluminum (Al), iron (Fe), titanium (Ti), manganese (Mn), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba), lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), and lead (Pb) in glass samples.

1.3 This procedure is applicable to irregularly shaped samples as small as 200 micrograms, for the comparison of fragments of a known source to the recovered fragments from a questioned source. These elements are present in soda lime and borosilicate glass in $\mu\text{g/L}$ to % levels.

1.4 This procedure is applicable to other elements, other types of glass, and other concentration ranges with appropriate modifications of the digestion procedure (if needed for full recovery of the additional elements), calibration standards and the mass spectrometer conditions. Calcium and potassium, for example, could be added to the list of analytes in a modified analysis scheme. Alternative methods for the determination of concentrations of elements in glass are listed in the references.

1.5 For any given glass, approximately 40 elements are likely to be present at detectable concentrations using this procedure with minor modifications. The element set stated here is an example of some of these elements that can be detected in glass and used for forensic comparisons.

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

1.7 *This standard cannot replace knowledge, skills, or abilities acquired through education, training, and experience and is to be used in conjunction with professional judgment by individuals with such discipline-specific knowledge, skills, and abilities.*

1.8 *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.*

1.9 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*³

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

3. Summary of Test Method

3.1 The glass fragments are digested using a mixture of hydrofluoric, nitric and hydrochloric acids. Following acid digestion, the samples are taken to dryness to eliminate most of the silicate matrix and the excess acids. Then an internal

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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.

standard [rhodium (Rh)] is added as the samples are reconstituted in nitric acid. Dilutions may be utilized to quantitate those elements that are present in higher concentrations.

3.2 An inductively coupled plasma mass spectrometer is used to measure the concentrations of the elemental suite listed in 1.2. The instrument is adjusted for maximum sensitivity, best precision and to minimize oxides and doubly charged ion interferences. The instrument is then calibrated per manufacturer recommendations, using multi-elemental calibration standards with the same internal standards as that added to the samples.

3.3 Reagent blanks are measured along with the samples because detection limits are usually limited by the background signals generated by the reagent blanks. The limits of detection of the method are expected to be between 0.5 µg/L and 25 µg/L for most elements.

4. Significance and Use

4.1 This technique is destructive, in that the glass fragments may need to be crushed, and digested in acid.

4.2 Although the concentration ranges of the calibration curves shown in **Appendix X1** are applicable to soda lime and borosilicate glass, this method is useful for the accurate measurement of element concentrations from a wide variety of glass samples.

4.3 The determination of the element concentrations in glass yields data that can be used to compare fragments.

4.4 It should be recognized that the method measures the bulk concentration of the target elements. Any extraneous material present on the glass that is not removed before digestion can result in inaccurate concentrations of the measured elements.

4.5 The precision and accuracy of the method should be established in each laboratory that employs the method.

5. Apparatus

5.1 *ICP-MS*—An Inductively Coupled Plasma Mass Spectrometer (ICP-MS) instrument is employed. Since there are several manufacturers for ICP-MS instruments, the instrument maker, model, configuration, and major operational parameters should be noted within the analysis results.

5.2 *Standard Reference Glasses*—A minimum of two different standard reference glasses of known elemental composition should be used. Examples suitable for this analysis include NIST 1831 and NIST 612 Reference Glasses.⁴

5.3 *Non-Glass Laboratory Ware*.

5.4 *Micro-Balance*—A microbalance with a precision of ±1 µg or better is necessary for the accurate weighing of the glass samples.

5.5 *High Purity Reagents*—ICP-MS grade acids and reagents shall be used for digestion and dilution.

5.6 *Laboratory Oven or Dry Bath Block*.

5.7 *Micropipettes*.

5.8 *Fume Hood*.

6. Hazards

6.1 Hydrofluoric acid (HF) is corrosive to all body tissues and bone. Skin, eye or respiratory contact with HF presents a significant health hazard that requires immediate first aid and possibly specialized medical care. Extreme care must be exercised in the presence of this acid. Calcium gluconate gel should be kept in the immediate area of HF use in the event of a potential skin exposure. See the chemical manufacturer's Safety Data Sheet for more information.

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 radio-frequency 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.

7. Sample Preparation

7.1 The sample set for analysis shall include all known samples, questioned samples and at least two standard reference glasses. Prior to crushing the glass sample for the digestion, soak samples in concentrated HNO₃, rinse 3 times with high purity water, and allow the samples to dry.

7.2 Crush the samples between clean polymeric materials, such as polystyrene weighing boats or glassine sheets, taking care not to puncture the materials.

7.3 Accurately weigh approximately 2 to 3 mg of each sample using a microbalance (with a precision of ±1 µg or better) and quantitatively transfer into a labeled non-glass tube with a cap. At least three weighings per glass source shall be made for a minimum of three analytical samples per glass source for digestion. Prepare empty labeled non-glass tubes for reagent blanks.

7.4 All volumes are delivered using micropipets. Add concentrated hydrofluoric acid, concentrated hydrochloric acid, and concentrated nitric acid to each tube to make a 2 to 1 to 1 mixture of the acids in the tubes.

7.5 Cap and vortex mix the tubes. The tubes may be placed in an ultrasonic bath to assist in the digestion for approximately one hour. Uncap the tubes and place in a dry bath block or an oven, at 80°C or greater (but below the softening temperature of the digestion tubes), until dry.

7.6 Reconstitute the samples by adding 500 µL of 50 % HNO₃ (8.0 mol/L). Recap the tubes and vortex mix.

7.7 The tubes may be placed in an ultrasonic bath for at least one hour or left to stand overnight.

7.8 Add 50 µL of a 10 mg/L Rh internal standard solution and 4450 µL of ultrapure water to each tube and vortex mix contents. Each tube will contain a 5 mL solution with 100 µg/L Rh internal standard in 5 % HNO₃.

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

8. Instrument Set-Up and Calibration

8.1 Tune the instrument prior to the analysis using the manufacturer's recommendations covering the mass range of the identified elements. The instrument shall be adjusted for maximum sensitivity, best precision, and to minimize oxides and doubly charged ion interferences.

8.2 Prepare calibration standards from pure element standards traceable to accepted metrological sources (NIST, etc.) covering the expected range of concentrations of the glass samples.

8.3 Prepare two calibration curves as well as two check standards. The first calibration curve shall consist of ^{24}Mg , ^{27}Al , ^{47}Ti , ^{57}Fe , ^{55}Mn , ^{88}Sr , ^{90}Zr , ^{138}Ba , and $^{206, 207, 208}\text{Pb}$ with a concentration range of 0.0, 1.0, 10.0, 50.0, 75.0, and 150.0 $\mu\text{g/L}$. The second calibration curve shall consist of ^{85}Rb , ^{139}La , ^{140}Ce , ^{146}Nd , ^{148}Sm with a concentration range of 0.0, 0.1, 0.5, 1.0, 5.0, and 50 $\mu\text{g/L}$. An internal standard of 100 $\mu\text{g/L}$ Rh shall be used in each standard sample.

8.4 The check standard (continuing calibration verification or CCV) for the element standards calibration shall be 50.0 $\mu\text{g/L}$ for the first group and 5.0 $\mu\text{g/L}$ for the second group.

8.5 Analyze the standard samples using the ICP-MS and calibration curves established for each group of elements. Analyze the continuing calibration verification (CCV) samples. The system should be recalibrated any time that the CCV falls outside the acceptable parameters established by the laboratory or analyst for this procedure.

9. Sample Analysis

9.1 Analyze a reagent blank with every sample set.

9.2 Analyze blanks between replicate groups.

9.3 Analyze two Standard Reference Glasses (NIST 1831, NIST 612, etc.) as a part of the sample set.

9.4 Analyze all blanks and digested glass samples using the instrument parameters established during tuning. The data are compared to the calibration curves, concentration values are determined, and corrected for the weight of the glass sample used. Final concentration values should be reported as milligram of element per kilogram of glass (mg/kg).

10. Quality Control

10.1 *Continuing Calibration Verification (CCV)*—After measuring the standards and periodically throughout the analysis, a CCV sample is measured to determine if the calibration is valid. The CCV sample is another solution containing all of the elements of interest at a known concentration (50.0 $\mu\text{g/L}$ and 5.0 $\mu\text{g/L}$). The system is recalibrated any time one or more element concentrations measured for the CCV sample fall outside the acceptable concentration ranges for the actual concentration of the elements in the CCV. The acceptable ranges of the concentrations of the elements in the CCV and the frequency of CCV sample measurements should be determined by each laboratory using this method.

10.2 *Method Detection Limit (MDL) and Limit of Quantitation (LOQ)*—The MDL for each element is determined by

measuring the concentrations of the elements of interest in three procedure blanks on two non-consecutive days. The MDL is the standard deviation of the concentration of each element in the three procedure blanks times three. The LOQ is the standard deviation of the concentration of each element in the three procedure blanks times ten. To calculate these limits of detection and quantitation, the average from the results for the two days is taken.

NOTE 1—Table X2.1 illustrates the values for MDL, LOQ, and range of concentrations found in a set of 50 soda-lime glass samples all expressed as $\mu\text{g/L}$ of the elemental concentration in the final solution.

10.3 *Accuracy of Standard Reference Material (SRM)*—SRMs with known concentrations of elements in glass are measured to assess the accuracy of the method. If one or more element concentrations fall outside of the acceptable ranges of concentrations (as determined by each laboratory), the sample analysis can yield inaccurate concentrations. Corrective actions should be taken to address the source of the inaccuracy prior to additional analysis.

11. Calculation and Interpretation of Results

11.1 The procedure below shall be followed to conduct a forensic glass comparison when using the recommended match criteria (17-19).

11.1.1 For the Known source fragments, using a minimum of 3 measurements, calculate the mean for each element.

11.1.2 Calculate the standard deviation for each element. This is the Measured SD.

11.1.3 Calculate a value equal to 3 % of the mean for each element. This is the Minimum SD.

11.1.4 Calculate a match interval for each element with a lower limit equal to the mean minus 4 times the SD (Measured or Minimum, whichever is greater) and an upper limit equal to the mean plus 4 times the SD (Measured or Minimum, whichever is greater).

11.1.5 For each Recovered fragment, using a minimum of 3 measurements, calculate the mean concentration for each element.

11.1.6 For each element, compare the mean concentration in the Recovered fragment to the match interval for the corresponding element from the Known fragments.

11.1.7 If the mean concentration of one (or more) element(s) in the Recovered fragment falls outside the match interval for the corresponding element in the Known fragments, the element(s) does not "match" and the glass samples are considered distinguishable.

11.2 The expected error rates when using the recommended criteria for the comparison of elemental composition of glass are reported in the literature (17-19). However, the method is not meant to be exclusive, and other methods that provide similar or better performance in terms of error rates than the recommended method can be used in the practice.

12. Precision and Bias

12.1 An interlaboratory study was conducted in 2001. Each of four laboratories tested four standard reference glasses using 5 replicate sample measurements of NIST 612, NIST 614, NIST 621, and NIST 1831.