Designation: E2330 – 12

Standard Test Method for Determination of Concentrations of Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Forensic Comparisons[1]

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.

1.2 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 ppb 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 This guide cannot replace knowledge, skill, or ability acquired through appropriate education, training, and experience and should be used in conjunction with sound professional judgment.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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 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 identified elements (1.1). The instrument should be adjusted for maximum sensitivity, best precision and to minimize oxides and doubly

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[2] 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.

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 ppb and 25 ppb in solution for most elements.

4. Significance and Use

4.1 This technique is destructive, in that the glass fragments may need to be crushed, and must be 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 may 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 ICP-MS instrument is employed.

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.

5.3 *Non-Glass Laboratory Ware*—for digestion.

5.4 *Micro-Balance,* with a precision of ±1 µg or better.

5.5 *High Purity Reagents,* ICP-MS grade acids and reagents for digestion and dilution.

5.6 *Laboratory Oven or Dry Bath Block,* for digestion.

5.7 *Micropipettes,* used for the addition of reagents.

5.8 *Fume Hood,* for work with acids and removal of HF fumes.

6. Sample Preparation

6.1 The sample set for analysis will 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 HNO_3, rinse 3 times with high purity water, and allow the samples to dry.

6.2 The samples are crushed between clean polymeric materials, such as polystyrene weighing boats or glassine sheets, taking care not to puncture the materials.

6.3 Approximately 2 to 3 mg of each sample should be accurately weighed using a microbalance (with a precision of ±1 µg or better) and quantitatively transferred into a labeled non-glass tube with a cap. At least three weighings per glass source should be made for a minimum of three analytical samples per glass source for digestion. Empty labeled non-glass tubes should be prepared for reagent blanks.

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

6.5 The tubes are capped, vortex mixed, and placed in an ultrasonic bath to assist in the digestion for approximately one hour. The tubes are then uncapped and placed in a dry bath block or an oven, at 80°C or greater (but below the softening temperature of the digestion tubes), and taken to dryness.

6.6 The samples are reconstituted by adding 500 µL of 50 % HNO_3 (8.0 $molL^{-1}$). The tubes are re-capped.

6.7 The tubes are vortex mixed and ultrasonicated for at least one hour or left to stand overnight.

6.8 Add 50 µl of a 10 ppm 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 ppb Rh internal standard in 5 % HNO_3 (8.0 $molL^{-1}$).

7. Instrument Set-Up and Calibration

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

7.2 Calibration standards are prepared from pure element standards traceable to accepted metrological sources (NIST, etc.) covering the expected range of concentrations of the glass samples.

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

7.4 The check standard (continuing calibration verification or CCV) for the element standards calibration is 50.0 ppb for the first group and 5.0 ppb for the second group.

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

8. Sample Analysis

8.1 A reagent blank will be analyzed with every sample set.

8.2 Blanks will be analyzed between replicate groups.