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

This standard is issued under the fixed designation E 2330; 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 This test method covers a procedure for elemental analysis of magnesium (Mg), aluminum (Al, titanium (Ti), manganese (Mn), gallium (Ga), rubidium (Rb), strontium (Sr), zirconium (Zr), antimony (Sb), barium (Ba), lanthanum (La), cerium (Ce), samarium (Sm), hafnium (Hf) and lead (Pb) in the bulk of glass samples (irregularly shaped and 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 ngg^{-1} to % levels. Alternative methods for the determination of elemental analysis of glass are listed in the references. This procedure may also be applicable to other elements, other types of glass, or other concentration ranges with appropriate modifications of the digestion procedure (if needed for full recovery of the additional elements) and the mass spectrometer conditions. The addition of calcium and potassium, for example, could be added to the list of analytes in a modified analysis scheme.

1.2 *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. Summary of Test Method

2.1 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 is added as the samples are reconstituted in nitric acid. Dilutions may be utilized to quantitate those elements that are present in higher concentrations.

2.2 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 charged ion interferences. The instrument is then calibrated per

manufacture recommendations using multi-elemental calibration standards with the same internal standards (Rh and Sc) as that those added to the samples.

2.3 Reagent blanks are measured along with the samples as 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 $0.5 \ ngg^{-1}$ and $25 \ ngg^{-1}$ in solution for most elements.

3. Significance and Use

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

3.2 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 trace elements from a wide variety of glass samples.

3.3 The determination the elemental concentrations in glass allows for additional data that can be compared between fragments. A standardized, validated method can aid in the interchange of data between laboratories.

3.4 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 a measurably different concentration of the elements.

3.5 The precision and accuracy of the method should be established in each laboratory that employs the method. Confidence intervals or a similar statistical quality statement should be quoted along with any reported concentration value.

4. Apparatus

4.1 *ICP-MS*—An ICP-MS instrument is employed. Since there are many manufacturers, the specification of the instrument should be noted within the analysis results.

4.2 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. The instrument is then calibrated per manufacture recommendations

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[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.
Current edition approved Aug. 1, 2004. Published August 2004.

using multi-elemental calibration standards with the same internal standard as that added to the samples.

4.3 *Replicates*—The minimum number of measurement replicates per sample should be three with consideration for additional measurements, if practicable

4.4 *Standard Reference Glasses*—A minimum of two different reference glasses of known elemental composition should be used.

5. Calibration

5.1 Two calibration curves as well as two check standards are used (Appendix X1). The calibration standards must be NIST traceable.

5.2 For the trace element standards calibration curve, Rh (50 ngg^{-1}) is used as an internal standard and the elements are grouped according to the expected concentrations. The first group consists of Mg, Ti, Mn, Sr, Zr, Sb, Ba and Pb with a concentration range of 0 to 150 ngg^{-1}. The second group consists of Ga, Rb, La, Ce, Sm and Hf with a concentration range of 0 to 50 ngg^{-1} ppb.

5.3 The check standard for the calibration is 50 ngg^{-1} for the first group and 5 ngg^{-1} for the second group.

5.4 The high standards calibration curve has Sc (60 ngg^{-1}) as an internal standard and is composed of three concentrations levels of Mg, Al, and Ba from 0 to 150 ngg^{-1}.

5.5 The check standard for the high standard calibration curve is 60 ngg^{-1} in all elements including Sc.

5.6 The system calibration must be checked daily (or on the days the instrument is in use for analysis) and prior to the performance of an analysis, as well as during the analysis after every ten samples. This is accomplished by the analysis of the check standards as a continuing calibration verification (CCV).

5.7 The system is recalibrated any time that the control falls outside the acceptable parameters established by the laboratory or analyst for this procedure (10 % tolerance is recommended).

5.8 *Method Detection Limit (MDL) and Limit of Quantitation (LOQ)*—The limits of detection of the method (MDL)are determined for each element by measuring the three procedure blanks on two non-consecutive days. Multiply by three the standard deviation (three instrumental replicates) of the measured intensities calculated by the calibration curve for that element in the day that it is measured. To calculate the limits of quantitation for the method (LOQ), multiply by ten the standard deviation (three instrumental replicates) of the measured intensities calculated by the calibration curve for that element in the day that it is measured. The measured intensities must be converted to concentration units using the appropriate calibration curve and the standard deviations calculated from the concentrations. 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 expected values for a set of 50 soda-lime glass samples all expressed as ngg^{-1} of the elemental concentration in the final solution

6. Procedure

6.1 Prior to crushing the glass sample for the digestion, wash samples separately in MeOH for 10 min and rinse 3 times with high purity water (>18 MΩ-cm). Wash in 1.6 molL^{-1} HNO$_3$ for 30 min, rinse 3 times with high purity water and air-dry overnight.

6.2 The samples are crushed between clean polystyrene weighing boats using a pestle, taking care not to puncture the boats.

6.3 Approximately 2 to 3 mg of each sample should be accurately weighed (with a precision of ± 1μg or better) and quantitatively transferred into a labeled polypropylene test tube with a cap. Each sample should be weighed in triplicate for three determination for each glass exhibit.with a precision of ± 1 μg or better.

6.4 All volumes are delivered using pipetters. The following mixture is added to each sample, and standards: 150 μL of concentrated HNO$_3$ (16 molL^{-1}), 300 μL of concentrated HF (29 molL^{-1}), and 150 μL of concentrated HCl (12 molL^{-1}). This acid mixture is also used to prepare the reagent blanks.

Note 2—All reagents are at least trace metal quality for ICP-MS.

Note 3—Normally, the mixture turns pale yellow, and if not, the acid reagents may have lost their strength and should be replaced before adding them to the samples.

6.5 The tubes are capped, vortex mixed, and placed in an ultrasound bath to assist in the digestion. The tubes are then uncapped and placed in a dry bath block or an oven, at 80°C (or greater but below the temperature of the softening of the digestion tubes), and taken to dryness (about 24 h).

6.6 The samples are reconstituted by adding 800- μL of HNO$_3$ (4.0 molL^{-1}), 20 μL of an internal standard Rh stock solution (10 μgg^{-1} in HNO$_3$ 0.8 molL^{-1}) and 680 μL of high purity water and the tubes are capped.

6.7 The tubes are vortex mixed and left to stand overnight.

6.8 A 2.500 mL volume of high purity water is added, the tubes are capped and vortex mixed. A 50 μL aliquot is removed and the remaining digest solution (undiluted) is analyzed using the trace element standardscalibration curve (or curves).

Note 4—The 50 μL aliquot of the above solution is transferred to a polypropylene test tube. A 30 μL volume of a scandium (Sc) internal standard (10 gg-1 in 0.8 molL-1 HNO3) and 4.920 ml of 0.8 molL-1 HNO3 are added. The solution is vigorously mixed before analysis. This second dilution is analyzed for magnesium, aluminum, and barium with the high standards calibration curve.

7. Precision and Bias

7.1 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.

7.2 The bias and precision results for each of the glasses are tabulated in Appendix X3. The terms repeatability and reproducibility are used as specified in Practice E 177. The 95 % limits were calculated by multiplying the respective standard deviations by a factor of 2.8.

8. Keywords

8.1 forensic science; glass comparisons; glass measurement; trace elemental analysis