



Standard Test Method for Analysis of Heavy Metals in Glass by Field Portable X-Ray Fluorescence (XRF)¹

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1. Scope

1.1 This test method covers field portable X-ray fluorescence (XRF) spectrometric procedures for analyses of arsenic and lead in glass compositions using field portable energy dispersive XRF spectrometers.

1.2 The mass fraction range of arsenic within which this test method is quantitative is given in [Table 1](#). Scope limits were determined from the interlaboratory study results using the approach given in Practice [E1601](#).

1.3 The mass fraction range for which lead was tested is given in [Table 1](#). However, lead results cannot be considered quantitative on the basis of single-sample results because the precision performance is not good enough to allow laboratories to compare results in a quantitative manner.

NOTE 1—The performance of this test method was evaluated using results based on single-sample determinations from specimens composed of glass beads. One laboratory has determined that performance can be significantly improved by basing reported results on the mean of determinations from multiple samples to overcome inherent heterogeneity of elements in glass beads, especially the element lead. Additional information is provided in Section [17](#) on Precision and Bias.

1.3.1 To obtain quantitative performance, lead results must consist of the average of four or more determinations.

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. Some specific hazards statements are given in Section 7 on Hazards.*

¹ This test method is under the jurisdiction of ASTM Committee on Declarable Substances in Materials and is the direct responsibility of Subcommittee [F40.01](#) on Test Methods.

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2. Referenced Documents

2.1 ASTM Standards:²

- [D75/D75M Practice for Sampling Aggregates](#)
- [D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)
- [E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications](#)
- [E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials](#)
- [E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)
- [E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)
- [E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis](#)
- [E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method](#)
- [E1621 Guide for X-Ray Emission Spectrometric Analysis](#)
- [F2576 Terminology Relating to Declarable Substances in Materials](#)

2.2 ANSI Standard:³

- [N43.2 Radiation Safety for X-Ray Diffraction and Fluorescence Analysis Equipment](#)

2.3 AASHTO Standard:⁴

- [TP-97-11 Test Method for Glass Beads used in Pavement Markings](#)

3. Terminology

3.1 *Definitions*—Definitions of terms applying to X-ray fluorescence (XRF) and declarable substances appear in Terminologies [E135](#) and [F2576](#), respectively.

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.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

⁴ Available from American Association of State Highway and Transportation Officials (AASHTO), 444 N. Capitol St., NW, Suite 249, Washington, DC 20001, <http://www.transportation.org>.

TABLE 1 Scope Ranges for Quantitative Results

Element	Scope Lower Limit (mg/kg)	Scope Upper Limit (mg/kg)
Arsenic	240	2000
Lead	120	500

3.2 *Compton-matrix correction, n* —measured intensity of Compton or incoherent scattered radiation may be used directly to compensate for matrix effects or indirectly for the determination of the effective mass absorption coefficient to correct for matrix effects.⁵

3.2.1 *Discussion*—The compensation for matrix effects is based on a combination of sample preparation and experimental intensity data.

3.3 *Compton scatter, n* —inelastic scattering of an X-ray photon through its interaction with the bound electrons of an atom.

3.3.1 *Discussion*—This process is also referred to as incoherent scatter.

3.4 *fundamental parameters, FP, model, n* —model for calibration of X-ray fluorescence response, including the correction of matrix effects, based on the theory describing the physical processes of the interactions of X-rays with matter.⁶

3.5 *Acronyms:*

3.5.1 *EDXRF*—Energy dispersive X-ray fluorescence

3.5.2 *QC*—Quality control

3.5.3 *XRF*—X-ray fluorescence

4. Summary of Test Method

4.1 Portable handheld instruments are used to measure glass spheres, ground glass, cullet, fiberglass, and sheet glass for their contents of arsenic and lead. Samples of sheet glass can be measured directly. Samples that are not in sheet form are measured as is or after pulverizing to an appropriate particle size.

4.2 The samples of glass spheres or powders may be placed into disposable cups with a polymer film supporting the glass. The filled cup is measured from below through the polymer film.

4.3 The glass specimen may be analyzed in situ by using a handheld spectrometer positioned in contact with sheet glass or the contents of a larger container, for example, a bulk shipping container.

4.4 The handheld XRF may be used while the operator is holding the unit or by being mounted in a stand for safer, more convenient laboratory use. The two measurement options are discussed throughout this test method.

5. Significance and Use

5.1 Waste glass is currently recycled into various consumer products. This test method has been developed as a tool for

⁵ Andermann, G. and Kemp, J. W., “Scattered X-rays as Internal Standards in X-Ray Spectroscopy,” *Analytical Chemistry*, Vol 20, No. 8, 1958.

⁶ The algorithm used for the procedure is usually implemented in the instrument manufacturer’s software. Third-party software is available and may be used.

evaluation of heavy metals in glass to satisfy reporting requirements for maximum allowable content for some applications.

5.2 The ranges within which this test method is quantitative are given in **Table 1**.

5.3 For amounts of the analyte elements outside the ranges in **Table 1**, this test method provides screening results. That is, it provides an unambiguous indication that each element can be described as present in an amount greater than the scope upper limit or that the amount of the element can be described as less than the scope lower limit with a high degree of confidence.

NOTE 2—In general, when a quantitative result is obtained, the analyst can make a clear decision as to whether a material is suitable for the intended purpose. When the contents of elements of interest are outside the quantitative range, the analyst can still make a decision whether the amount is too high or whether additional analyses are required.

5.4 These methods can be applied to glass beads, plate glass, float glass, fiber glass, or ground glass. This test method has been validated for the ranges of matrix compositions that are summarized in **Table 2**.

5.5 Detection limits, sensitivity, and element ranges will vary with matrices, detector type, and other instrument conditions and parameters.

5.6 All analytes are determined as the element and reported as such. These include all elements listed in **Table 1**. This test method may be applicable to other glass matrices, additional elements, and wider concentration ranges provided the laboratory is able to validate the broadened scope of this test method.

6. Interferences

6.1 *Spectral Interferences*—These can occur for some elements as a result of partial or total line overlaps. These line overlaps can result from scattered characteristic lines from the target of the X-ray tube or by X-ray fluorescence from atoms in the specimen. Spectral interference can also be the result of escape peaks from the solid-state detector. See Guide **E1621** for a full discussion of models used to correct for these effects. In this particular case, the most obvious line overlap is the overlap of As K- $L_{2,3}$ (As K $\alpha_{1,2}$; 10.53 keV) on Pb L_{3-M_5} (Pb $L\alpha_1$; 10.55 keV) and vice versa. The energy difference between these two lines is about 0.02 keV, which cannot be resolved with the detectors used. The emission lines of these two elements will appear as a single peak. However, both As and Pb have alternative lines that can be used for analysis. For Pb, the use of the doublet Pb $L_{2,3-M_4,N_5}$ (Pb $L\beta_{1,2}$; 12.61 keV) is highly recommended. This line has virtually the same sensitivity as the Pb L_{3-M_5} line. For As, the As K- $M_{2,3}$ (As K $\beta_{1,3}$; 11.72 keV) can be used; its sensitivity is about 20 % of the more intense As K- $L_{2,3}$ line. It is possible to determine the net intensity of Pb L_{3-M_5} based on the intensity of Pb $L_{2,3-M_4,N_5}$ (this implies determining a proportionality factor between the

TABLE 2 Matrix Components and Ranges

Oxide	Scope Lower Limit, %	Scope Upper Limit, %
SiO ₂	58	80
Al ₂ O ₃	1	10
Na ₂ O	3	15
CaO	6	20
MgO	1	5

two lines on specimens with no or varying amounts of As). This can then be used to calculate the intensity of As K-L_{2,3}.

6.2 In EDXRF, the possibility exists that two photons are seen and treated as a single one by the counting electronics. When that happens, they appear as a single photon with an energy corresponding to the sum of the energies of the individual photons. This phenomenon is called the sum-peak. For this effect to be significant, the total count rate must be high; and (at least) one element must be present at a relatively high level; and the element concerned must have a high yield. In the current method, the presence of e.g. iron at high levels could lead to a sum-peak of 2 Fe K-L3 (6.4 keV) photons, with an energy of about 12.6–12.8 keV - this corresponds to the energy of Pb L_{2,3}-M_{4,5}. The software provided by the manufacturer must correct for this effect; otherwise the intensity (and thus the contents) of Pb L_{2,3}-M_{4,5} is overestimated.

6.3 *Matrix Interferences*—Some of the X-rays generated within the sample will interact with atoms in the matrix. As a result of such interactions, the emitted intensity of the analyte depends on the amount of the analyte in the sample and, to a lesser, but measurable degree, on the amounts of other elements. The magnitude of such matrix interferences is most pronounced for elements that are present in high concentrations. Several mathematical models, such as the fundamental parameter model, exist for the correction of such effects; see Guide E1361 for a full discussion. Typically, these matrix correction models require that the net intensities are free from line overlap effects. In practice, the approach chosen depends upon the manufacturer.

6.4 Float glass is heterogeneous because one side is coated with tin. Differential absorption can bias the results.

7. Apparatus

7.1 *EDXRF Spectrometer*—designed for X-ray fluorescence analysis with energy dispersive selection of radiation. Any EDXRF spectrometer can be used if its design incorporates the following features.

7.1.1 *Source of X-Ray Excitation*—capable of exciting the recommended lines, typically an X-ray tube. The recommended lines are shown in Table 3.

7.1.2 *X-Ray Detector*—An energy resolution of better than 250 eV at Mn K-L_{2,3} has been found suitable for use in this test method.

7.1.3 Signal conditioning and data-handling electronics include the functions of X-ray counting and peak processing.

7.2 The following spectrometer features and accessories are optional.

7.2.1 *Beam Filters*—used to make the excitation more selective and reduce background count rates.

7.2.2 *Drift Correction Monitor(s)*—Because of instability of the measurement system, the sensitivity and background of the spectrometer may drift with time. Drift correction monitors may be used to correct for this drift. The optimum drift correction monitor specimens are permanent materials that are stable with time and repeated exposure to X-rays.

7.3 Reference Materials:

7.3.1 Purchased certified reference materials, and

7.3.2 In-house reference materials that were analyzed by at least two independent methods.

7.4 Consumables:

7.4.1 Disposable latex or nitrile gloves,

7.4.2 Methanol or isopropyl alcohol,

7.4.3 Deionized water,

7.4.4 XRF sample cups,

7.4.5 Lint-free wipes, and

7.4.6 Polymer film, including, but not limited to polyimide, polyester, and polypropylene.

8. Hazards

8.1 Safety practices shall conform to applicable local, state, and national regulations. For example, personal monitoring devices and periodic radiation surveys may be required.

8.2 *Dust Mask*—When this test method is performed on powder samples, it may be advisable to use a dust mask.

8.3 *Gloves*—The use of powder-free polymer gloves is recommended to prevent contamination of sample surfaces by body oils and other substances.

9. Sampling

9.1 Users should develop plans to determine if the measured specimens are representative of a larger quantity of material. Refer to AASHTO TP-97-11 or Practice D75/D75M for examples of sampling procedures for quantities greater than 45 kg.

9.2 For laboratories having small quantities of material, three replicate measurements may be taken to obtain information on homogeneity. If the range of three results is greater than the repeatability limit of this standard test method, there may be evidence for statistically significant heterogeneity. The analyst may measure more samples and note standard deviation.

10. Preparation of Test Specimens

10.1 Treat reference materials and test specimens for each method exactly the same way to ensure reproducible results. Samples may be analyzed with little sample preparation, if calibration standards and specimens are in the same form.

10.2 *Loose Beads*—For loose beads, simply place them in sample cups with polymer film. Samples and standards should be of comparable particle size for presentation to the spectrometer. The cup should be filled to a depth greater than 6 mm to achieve infinite thickness for arsenic and lead. The sample cup is placed in the measurement position of the EDXRF instrument for measurement.

TABLE 3 Analytical Lines for Analysis of Arsenic and Lead

	Analyte	
	Arsenic	Lead
Preferred Line	As K-L _{2,3} (As K $\alpha_{1,2}$; at 10.53 keV)	Pb L _{2,3} -M _{4,5} (Pb L $\beta_{1,2}$; at 12.61 keV)
Second Choice Line	As K-M _{2,3} (As K $\beta_{1,3}$; at 11.72 keV)	

10.3 Plate or Float Glass—Plate or float glass may be placed in the X-ray beam of the EDXRF for measurement. For plate or float glass, if the sheet is at least 6 mm thick and covers the entire beam aperture of the instrument, direct measurements can be made by placing the EDXRF on the sample or setting the sample to be in the instrument beam.

10.3.1 Provided it is known that multiple pieces are of the same composition, more than one piece of glass may be stacked to obtain the minimum thickness.

10.3.1.1 Although the results will be biased, the individual sheets can be measured to verify that they are the same composition before they are stacked.

10.3.2 For float glass, the air side is measured, as significant and varying quantities of tin can be picked up from the tin bath used in production. EDXRF may be used to determine which side was exposed to the tin bath and then the analysis shall be taken from the airside. Alternatively, the tin side can be determined by observing the fluorescent glow emitted from the tin side when the glass is exposed to a black light. Float glass can be ground to minimize interference.

10.4 Fiberglass—Fiberglass is chopped and then poured into a disposable cup with polymer film to a depth greater than 6 mm for analysis. Samples and standards should be in the form of glass fibers of comparable length and diameter for presentation to the spectrometer. The sample cup is placed in the measurement position of the EDXRF instrument for analysis.

10.5 Ground Glass—Crushed, ground, or powdered glass samples may originate from beads, float, fiberglass or plate glass. Ground or powdered glass samples shall be prepared in the same manner as the glass beads to give maximum consistent particle size of 1680 micron (U.S. mesh sieve size 12). The ground glass shall be poured into a sample cup with polymer film to a depth greater than 6 mm and then analyzed. Hence, if standards are in the form of ground glass, samples of glass to be analyzed may be ground to match the form of the standards.

11. Preparation of Apparatus

11.1 Turn on the analyzer and allow it to warm up and stabilize in accordance with manufacturer's recommendation.

11.2 Follow the manufacturer's recommendation to set the optimum measurement conditions (such as X-ray tube high voltage and current, primary beam filters and so forth) to measure the count rates of preferred analytical lines of arsenic and lead (see [Table 1](#), Sec. 7.1.1) or select the appropriate manufacturer supplied or laboratory prepared calibration.

11.3 Determine a minimum measurement time resulting in a maximum counting statistical error (CSE) at one sigma of 10 % relative for a specimen containing As and Pb at a level close to the specification or regulatory limit. This shall be performed for both arsenic and lead and for each anticipated sample/matrix type.

11.3.1 The required measurement time for an individual analyte (As or Pb) can be calculated by using [Eq 1](#):

$$t \geq \left(\frac{100}{CSE\%} \right)^2 \cdot \frac{1}{R} + \left(\frac{100}{CSE\%} \right)^2 \cdot \frac{2 \cdot BGD}{R^2} \quad (1)$$

where:

R = net count of Pb or AS X-rays in counts per second (cps) measured for time, t ,
 t = counting time in seconds, s,
 BGD = count rate of background under the Pb or As peak in cps, measured for time, t , and
 CSE = relative error of counting statistics, %

11.3.2 When the background count rate, BGD , is much less than the net count rate, R , the second term in [Eq 1](#) may be omitted and then the product of R and t equals the total number of net counts accumulated under the Pb peak in EDXRF measurements. This time corresponds to a measuring time resulting in collection of >100 counts after accounting for background.

11.3.3 In cases of instruments precalibrated by the manufacturer, measure specimens containing As and Pb at the levels close to specification or regulatory limit for as long as it takes the measurement error reported by the instrument for each analyte at one sigma level to be <10 % relative to the value measured. the measurement time thus determined shall be used for subsequent tests.

11.4 Verify the Limit of Detection—The limit of detection, L_D , shall be estimated for each analyte, As and Pb, and for each anticipated sample/matrix type and measurement conditions by the use of [Eq 2](#):

$$L_D = 3 \cdot s \quad (2)$$

where:

s = standard deviation of a series of at least seven measurements of an arsenic and lead-free sample.

11.4.1 For optimum results, the L_D should be less than 30 % of the specification or regulatory limit or of the laboratory's action limit, whichever is less.

NOTE 3—Longer measurement time may be necessary for some instruments to achieve performance stipulated in [11.3](#) and [11.4](#). Relative error of measurement in EDXRF decreases twofold for each fourfold extension of measurement time. Therefore, the reduction of error obtained at 200-s measurement time by a factor of two would require measurement time of 800 s, which would significantly reduce the number of samples that could be measured.

12. Calibration

12.1 Calibration—The manufacturer of the spectrometer may provide the instrument calibration. In this case, verification of the calibration is required at the time of initial application, periodically during use, and after major repairs ([12.4](#)). If this is not the case, use one of the described calibration methods: an empirical calibration ([12.2](#)) or an FP calibration ([12.3](#)). Both methods rely on the use of a set of known standards or certified reference materials or both (see also [7.3](#)).

12.2 Empirical Calibration—Prepare or obtain a set of calibration standards that cover the range of interest of each analyte prepared in the matrix of interest. Standards that contain multiple analytes are preferred. It is important to have standards with mass fractions that vary independently from one another and span the range of mass fractions expected in the unknown samples. To the extent that it is practical, avoid

having correlations by ensuring that the mass fractions of the different analytes do not vary in proportion to one another in the standards. Ensure that the low mass fraction of one analyte is combined with a high mass fraction of another analyte. It is important to have available several standards for each analyte when using an empirical calibration to provide enough degrees of freedom to determine the influence coefficients as well as the slope and intercept of the calibration curve for each analyte.

12.2.1 Select an appropriate calibration algorithm that is expected to represent adequately the relationship between known mass fractions and measured count rates.

12.2.2 Place each standard specimen in the X-ray beam and measure the net count rate of each element using the measurement conditions chosen in Section 6.

12.2.3 Measure each standard at least twice preferably with two separately prepared specimens.

12.2.4 For each analyte, follow the manufacturer's instructions to perform a regression of net count rate versus mass fraction. The net count rates may be divided by the Compton scatter count rate for the specimen (or the background count rate, if Compton scatter cannot be measured).

12.2.5 Include significant interelement effects (see Section 6) in the regression model by using influence coefficients as per 6.2 and Guide E1361.

12.2.6 If the spectrum processing options do not include corrections for peak overlaps, corrections shall be included in the regression model. If a FP calibration is not being used, proceed to Section 13.

12.3 FP Calibration:

12.3.1 Matrix correction procedures by FP are based on mathematical descriptions of the most important interactions between X-ray photons and matter. Calibration with FP can be done using very few standards because the only parameters to be determined are the slope and intercept of the calibration curve. At least one standard for each analyte shall be available. Corrections for interelement effects are done entirely from theory. Standards made from pure elements or compounds may be used, but best results are obtained when the matrix of the standards is similar to the matrix of the samples. Full details of FP models are described in Guide E1361.

12.3.2 Place each standard specimen in the X-ray beam and measure the net count rate of each element using the measurement conditions chosen in Section 9.

12.3.3 Measure each standard at least twice preferably with two separately prepared specimens. Omit outliers beyond one sigma significance and perform the regression on the remaining standards data.

12.3.4 For each analyte, follow the manufacturer's instructions to perform a regression of net count rate versus mass fraction. The net count rates may be divided by the Compton scatter count rate for the specimen (or the background count rate, if Compton scatter cannot be measured).

12.3.5 If the spectrum processing options do not include corrections for peak overlaps, corrections shall be included in the regression model. FP approaches are predicated on the assumption that the count rate data has already been processed to remove background and spectral interferences.

NOTE 4—FP methods often require the sum of the known or determined constituents or both of a sample to be 100 %. Typically, results may be improved when information about the matrix composition is known.

12.4 Verification of Calibration:

12.4.1 The calibration shall be verified by analyzing one or more reference materials, preferably of the same glass matrix as the materials on which analyses will be performed. Measure the reference materials immediately after completing an empirical calibration or a FP calibration.

12.4.2 When using precalibrated systems, run the reference materials before measuring unknowns for the first time.

12.4.3 Determine the mass fractions in one or more quality control samples. The determined mass fraction from these measurements shall be in agreement with the known (certified) value. To test for a bias, use Eq 3:

$$\Delta_c = \sqrt{2s^2 + U^2} \quad (3)$$

where:

Δ = absolute value of the difference between the result and the known value,

Δ_c = critical values for detecting a bias,

s = repeatability standard deviation of measurement using the spectrometer, and

U = expanded uncertainty of the known value of the analyte in the reference material.

12.4.3.1 A bias is detected when $\Delta > \Delta_c$. If a bias is detected, an investigation shall be carried out to find the root cause.

12.5 Drift Monitors and Quality Control (QC) Samples:

12.5.1 When using drift correction, measure the count rates of the drift correction monitors in the same manner as the calibrants with the exception of counting times. The monitors' compositions and the count time for measurement of a monitor shall be optimized to achieve a minimum of 40 000 counts for each element for %CSE = 0.5.

12.5.2 When using QC charts, measure the control samples in the same manner as the unknowns. At the time a method is implemented in the laboratory, measure each QC sample at least seven times. Construct control charts using these data. See 7.4. The repeatability data of the QC sample shall be checked against the precision statement in 17.2 to ensure that the performance of the laboratory is comparable to the intralaboratory repeatability established during validation of this test method.

13. Conditioning

13.1 Allow the instrument to stabilize according to manufacturer's guidelines.

13.2 Standards and specimens that are to be retained for an extended time before analysis commences should be stored in a controlled temperature and humidity (< 20 % relative humidity and 20 to 25°C).

13.3 Standards used in the field shall be protected from contamination. Specimens measured in situ need not be conditioned.

14. Procedure

14.1 Measurement of Unknown Specimens:

14.1.1 Place the specimen on the instrument or the instrument on the specimen and perform the measurement using the conditions chosen in Section 9.

14.1.2 Process the spectrum using the same procedure chosen in Sections 10 and 11, including the same processes for handling escape peaks, sum peaks, background modeling and subtraction, and spectral overlaps.

14.2 QC Sample:

14.2.1 To ensure the quality of the results, analyze one or more QC samples at the beginning and end of a batch of specimens or after a fixed number of specimens but at least once each day of operation (see 12.5.2).

14.2.2 Analysis of result(s) from these specimens should be carried out following Practice D6299 or laboratory specific control procedures. Drift correction or instrument calibration may be required if the QC sample result indicates an uncontrolled situation.

14.3 *Drift Correction*—When using drift correction, measure the drift correction monitors before analyzing samples. By comparing the current count rate of the drift correction monitors to the count rate at the time of the calibration, it is possible to calculate correction factors that are then used to correct for any drift in sensitivity. The use of the instrument manufacturer's drift correction procedure is recommended.

NOTE 5—Drift correction is usually implemented automatically in the manufacturer's instrument software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from one.

15. Calculation

15.1 Using the net count rates for a specimen and the calibration created in Section 12, calculate the results in units of milligram/kilogram. Typically, the calculations can be done using the instrument software.

16. Report

16.1 Report the following information:

16.1.1 *Unique Identification of the Sample*—This may vary according to company guidelines and test purposes,

16.1.2 The date and time of the test,

16.1.3 A reference to this standard test method (F2980),

16.1.4 The origin of the sample,

16.1.5 A description of the specimen type: for example, disk, granulate, and so forth,

16.1.6 A description of the specimen preparation, if any, and

16.1.7 Deviations from this test method, if any.

16.2 The results of this test shall be expressed to the nearest 1 mg/kg. Follow the relevant procedures in Practice E29.

16.3 If a result is outside of the scope ranges listed in Table 2, report the result as one of the following:

16.3.1 If the result is less than the lower scope limit, report <LL where LL = value of the lower scope limit, and

16.3.2 If the result is greater than the upper scope limit, report >UL where UL = value of the upper scope limit.

17. Precision and Bias

17.1 The precision of this test method is based on an interlaboratory study of ASTM F2980, Test Method for Analysis of Heavy Metals in Glass by Field Portable X-Ray Fluorescence (XRF), conducted in 2010. Each of 13 laboratories tested 6 different materials. Every “test result” represented an individual determination on a single sample on a given day, and all participants were asked to report triplicate test results. Practice E691 was followed for the design of the study and analysis of the data; the details are given in an ASTM Research Report.⁷

17.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the *r* value for that material; *r* is the interval representing the critical difference between two test results for the same material obtained by the same operator using the same equipment on the same day in the same laboratory.

17.1.2 Repeatability limits are listed in Table 4 and Table 5.

NOTE 6—Material E was not used in the setting of the scope range because the material was found to be too heterogeneous for that purpose. The results for Material E are reported herein because the material is useful for demonstration of biases in this test method.

17.1.3 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the *R* value for that material; *R* is the interval representing the critical difference between two test results for the same material obtained by different operators using different equipment in different laboratories.

17.1.3.1 Reproducibility limits are listed in Table 4 and Table 5.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:F40-1002. Contact ASTM Customer Service at service@astm.org.

TABLE 4 Arsenic (mg/kg)

Material	Average ^A X	Repeatability Standard Deviation <i>Sr</i>	Reproducibility Standard Deviation <i>SR</i>	Repeatability Limit <i>r</i>	Reproducibility Limit <i>R</i>
E	169	17	37	48	100
F	411	11	42	31	120
A	590	38	74	110	210
B	694	18	47	52	130
C	893	26	67	73	190
D	1697	65	150	180	420

^AThe average of the laboratories' calculated averages.

TABLE 5 Lead (mg/kg)

Material	Average ^A X	Repeatability Standard Deviation Sr	Reproducibility Standard Deviation SR	Repeatability Limit r	Reproducibility Limit R
E	81	24	34	67	94
A	120	14	21	39	59
C	143	15	28	43	81
F	188	12	31	35	88
D	195	16	41	46	115
B	388	24	69	68	194

^AThe average of the laboratories' calculated averages.

17.1.4 The terms repeatability limit and reproducibility limit are used as specified in Practice E177.

17.1.5 Any judgment in accordance with 17.1.1 and 17.1.2 would have an approximate 95 % probability of being correct.

17.1.6 Results in Table 4 for arsenic show the test method to be capable of producing quantitative results from a single sample for all materials tested because the repeatability standard deviation, s_r , is approximately 10 % relative to the mean result, in the worst case of material E.

17.1.7 Results in Table 5 for lead show the test method to be incapable of producing quantitative results from a single sample when the lead mass fraction is <188 mg/kg because the repeatability standard deviation, s_r , is greater than 10 % relative to the mean result below 188 mg/kg Pb.

17.1.8 Results in Table 4 for arsenic demonstrate that for all materials, except E, the reproducibility index is low enough to allow two laboratories to compare results quantitatively on the basis of the requirement of Practice E1601. Per Practice E1601, the minimum scope limit for arsenic is 240 mg/kg, which equals 2R for material F.

17.1.9 Results in Table 5 for lead demonstrate that for all materials the reproducibility index is too high to allow two laboratories to compare results quantitatively. For all materials, $2R \geq 50$ % relative to the mean result.

17.1.10 Using X-ray fluorescence spectrometry in a separate experiment, one laboratory demonstrated that lead can be significantly more heterogeneous in glass bead materials than arsenic.

17.1.10.1 Using a typical glass bead material (not one of the ILS materials), the laboratory performed 48 measurements of individual samples of beads placed into liquid cells equipped with polyester support film. Using nylon sieves, the beads were found to range in size from 100 to 400 μ m diameter.

17.1.10.2 The information in Table 6 demonstrates that the repeatability of individual results for arsenic is clearly better than for lead.

17.1.10.3 When results were designated to be the mean of multiple sample measurements, the repeatability standard deviations for all elements decreased as the number of measurements averaged together increased. Therefore, the precision of

results can be improved by averaging multiple measurements to form a single result.

17.2 Bias—At the time of the interlaboratory study, there were no accepted reference materials suitable for determining the bias for this test method. Therefore, an interlaboratory study was carried out using independent test methods to develop reference values for the materials used in the study.

17.2.1 Consensus values and uncertainty estimates are reported in Table 7 and Table 8 along with the differences, Δ , between the average values from Table 4 and Table 5 and the consensus values. The consensus mean values are the unweighted means of laboratory mean results wherein the laboratories used atomic spectrometric methods for $n = 1$ to $n = 6$ determinations for each material. The reported uncertainty estimates are expanded uncertainties, U , calculated as $U = ku_c$, where k is the expansion factor taken from the Student's t table for a confidence level of 95 % and the appropriate degrees of freedom, and u_c is a combined uncertainty at the level of one standard deviation calculated by adding in quadrature the pooled repeatability standard deviation from the participating laboratories and an estimate of the bias between laboratories and test methods.⁸

17.2.2 Bias estimates are represented by the difference, Δ , values in Table 7 and Table 8.⁹ Data for lead exhibit a positive bias at low mass fractions of between 10 and 30 mg/kg. Data for arsenic do not exhibit detectable biases. The trends are clearly seen in Fig. 1 and Fig. 2 that show the correlations between consensus values and average values. The error bars in these two figures represent the expanded uncertainty estimates for the consensus values and the repeatability standard deviations for the average XRF values.

17.3 The precision statement and bias statements were determined through statistical examination of 616 results from 13 laboratories on these 6 materials:

- 17.3.1 Sample A—OM 4-23-08 SI OPSS 1750,
- 17.3.2 Sample B—2465-97 O M 4-14-2008,
- 17.3.3 Sample C—AW MIL 6,
- 17.3.4 Sample D—CHINESE GB,
- 17.3.5 Sample E—OM 50-70, and
- 17.3.6 Sample F—OM 100-170 B10.

TABLE 6 Decrease of Repeatability Standard Deviation for Lead with Increase of the Number of Measurements Used as a Single Result

Number of measurements	2	3	4
% Decrease of s	25	41	50

⁸ Levenson, M. S., Banks, D. L., Eberhardt, K. R., Gill, L. M., Guthrie, W. F., et al, *J. Res. Nat. Inst. Stand. Technol.*, Vol 105, 2000, p 571.

⁹ Becker, D., et al., NIST (NBS) Special Publication 829, U.S. Government Printing Office, Washington D.C., 1992, 30 pp.

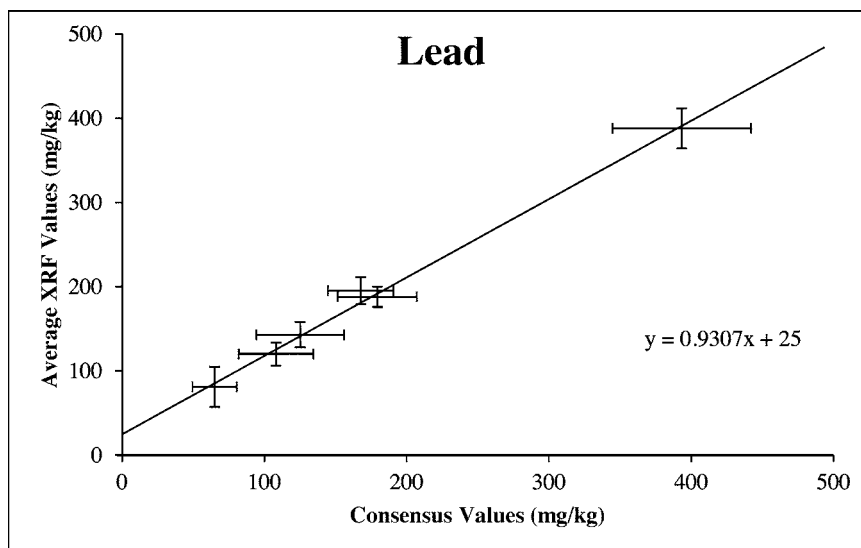


FIG. 1 Correlation for Lead Showing Positive Bias at Low Mass Fractions

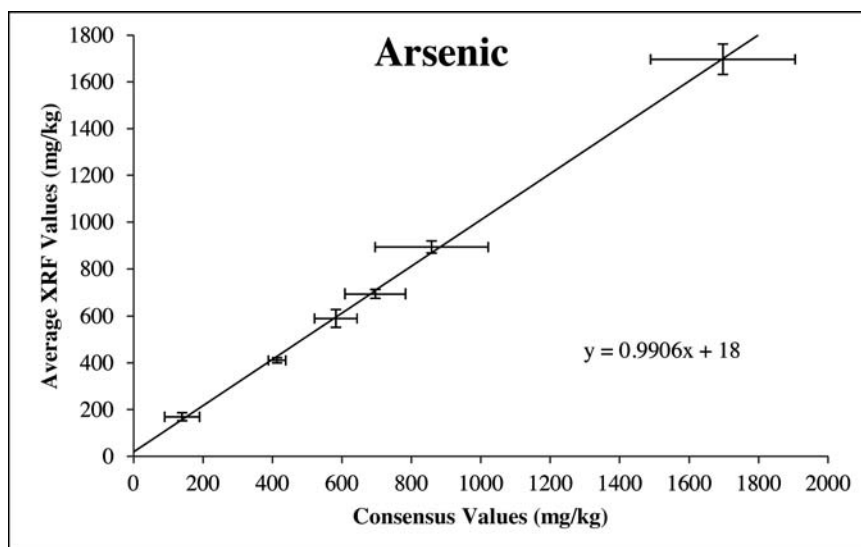


FIG. 2 Correlation for Arsenic Showing No Detectable Bias at Low Mass Fractions

TABLE 7 Arsenic (mg/kg)

Material	Consensus Mean	Expanded Uncertainty U	Expansion Factor k	Difference (Average-Mean) Δ
E	140	50	2.0	29
F	413	25	2.0	-2
A	583	61	2.2	7
B	696	87	2.4	-2
C	859	163	2.0	35
D	1697	208	2.3	0

TABLE 8 Lead (mg/kg)

Material	Consensus Mean	Expanded Uncertainty U	Expansion Factor k	Difference (Average-Mean) Δ
E	65	16	2.0	16
A	108	26	2.3	12
C	125	31	2.0	18
F	179	28	2.0	9
D	168	23	2.0	27
B	393	49	2.0	-5

17.4 To judge the equivalency of two test results, it is recommended to choose the material most similar in characteristics to the test material.

18. Keywords

18.1 EDXRF; energy dispersive; glass; X-ray; X-ray fluorescence; XRF



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