Designation: F2980 – 13

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

This standard is issued under the fixed designation F2980; 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 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.*

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 Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry
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

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

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

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 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 Lα_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,

TABLE 2 Matrix Components and Ranges

Oxide	Scope Lower Limit, %	Scope Upper Limit, %
SiO_2	58	80
Al_2O_3	1	10
Na_2O	3	15
CaO	6	20
MgO	1	5

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[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.

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 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,N_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,N_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.

TABLE 3 Analytical Lines for Analysis of Arsenic and Lead

	Analyte	
	Arsenic	Lead
Preferred Line	As K-$L_{2,3}$	Pb $L_{2,3}$–M_4, N_5
	(As $K\alpha_{1,2}$; at 10.53 keV)	(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)	

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.

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 anaticipated sample/matrix type.

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

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

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:

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

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).