



Designation: F2617 – 08<sup>ε1</sup>

# Standard Test Method for Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry<sup>1</sup>

This standard is issued under the fixed designation F2617; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Added research report footnote to Section 16 editorially in May 2009.

## 1. Scope

1.1 This test method describes an energy dispersive X-ray fluorescence (EDXRF) spectrometric procedure for identification and quantification of chromium, bromine, cadmium, mercury, and lead in polymeric materials.

1.2 This test method is not applicable to determine total concentrations of polybrominated biphenyls (PBB), polybrominated diphenyl ethers (PBDE) or hexavalent chromium. This test method cannot be used to determine the valence states of atoms or ions.

1.3 This test method is applicable for a range from 20 mg/kg to approximately 1 wt % for chromium, bromine, cadmium, mercury, and lead in polymeric materials.

1.4 This test method is applicable for homogeneous polymeric material.

1.5 The values stated in SI units are to be regarded as the standard. Values given in parentheses are for information only.

1.6 This test method is not applicable to quantitative determinations for specimens with one or more surface coatings present on the analyzed surface; however, qualitative information may be obtained. In addition, specimens less than infinitely thick for the measured X rays, must not be coated on the reverse side or mounted on a substrate.

1.7 *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.*

<sup>1</sup> 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.

Current edition approved Aug. 15, 2008. Published September 2008. DOI: 10.1520/F2617-08E01.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D883 Terminology Relating to Plastics
- D3641 Practice for Injection Molding Test Specimens of Thermoplastic Molding and Extrusion Materials
- D4703 Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets
- 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
- E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis
- F2576 Terminology Relating to Declarable Substances in Materials

## 3. Terminology

### 3.1 Definitions:

3.1.1 Definitions of terms applying to XRF, plastics and declarable substances appear in Terminology E135, Terminology D883 and Terminology F2576, respectively.

3.1.2 *Compton scatter*—the inelastic scattering of an X-ray photon through its interaction with the bound electrons of an atom; this process is also referred to as incoherent scatter.

3.1.3 *Rayleigh scatter*—the elastic scattering of an X-ray photon through its interaction with the bound electrons of an atom; this process is also referred to as coherent scatter.

<sup>2</sup> 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.

3.1.3.1 *Discussion*—The measured count rate of Compton and Rayleigh scattered radiation varies depending upon specimen composition and may thus be used to compensate for matrix effects. One option is to use the measured count rate of the Compton scatter in the same manner as the measured count rate of an internal standard element. Alternatively, the measured count rate of the Compton scatter or the Compton/Rayleigh scatter ratio may be used indirectly for estimating the effective mass absorption coefficient of the specimen, which is used to compensate for matrix effects. The concept of corrections based on the Compton scatter effect is discussed as an optional part of several calibration choices in this standard.

3.1.4 *fundamental parameters (FP) model*—a 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.

3.1.5 *homogeneous polymeric material*—polymeric material is considered homogeneous for XRF when the elemental composition is independent with respect to the measured location on the specimen and among separate specimens prepared from the same polymeric material.

3.1.6 *infinite thickness (or critical thickness)*—the thickness of specimen which, if increased, yields no increase in intensity of secondary X rays, due to absorption by the polymer matrix.

3.1.6.1 *Discussion*—This thickness varies with secondary X-ray energy, or wavelength.

3.2 *Abbreviations:*

3.2.1 *EDXRF*—energy dispersive X-ray fluorescence

3.2.2 *FP*—fundamental parameters

3.2.3 *PBB*—polybrominated biphenyl

3.2.4 *PBDE*—polybrominated diphenyl ether

## 4. Summary of Test Method

4.1 The optimum test sample is a smooth plaque or disk large enough to cover the viewed area of the spectrometer. Suitable specimens may be die-cut from extruded sheets, or molded from resin pellets, from powders or from granules.

4.2 The specimen is placed in the X-ray beam, and the appropriate region of its spectrum is measured to give the count rates or fluorescent intensities of lead, mercury, cadmium, chromium and bromine.

4.3 The EDXRF spectrometer is calibrated by one of several approaches including fundamental parameters and empirical, classical curve construction, with either empirical or theoretical influence coefficients, from measured polymer reference materials. The calibration may be performed by the manufacturer or by the user.

4.4 Choices of appropriate characteristic X-ray lines and spectrometer test conditions may vary according to each element and with factors such as detector response, concentration range and other elements present in the polymer matrix.

## 5. Significance and Use

5.1 This test method is intended for the determination of chromium, bromine, cadmium, mercury, and lead, in homogeneous polymeric materials. The test method may be used to

ascertain the conformance of the product under test to manufacturing specifications. Typical time for a measurement is 5 to 10 min per specimen, depending on the specimen matrix and the capabilities of the EDXRF spectrometer.

## 6. Interferences

6.1 *Spectral Interferences*—Spectral interferences result from the behavior of the detector subsystem of the spectrometer and from scattering of X rays by the specimen, by a secondary target or by a monochromator, if the spectrometer is so equipped. Overlaps among the X-ray lines from elements in the specimen are caused by the limited resolution of the detection subsystem. Depending upon the resolution of the detector system, the peaks from Zn, Br, Hg and Pb may overlap with one another. Peaks from Cd may overlap with peaks from Ca, Sn, or other elements. Interactions of photons and electrons inside the detector give rise to additional peaks in a spectrum known as escape peaks and sum peaks. Fundamental Parameters equations require that the measured net count rates be free from line overlap effects. Some empirical approaches incorporate line overlap corrections in their equations. Manufacturers' software may provide tools to compensate for overlapped peaks, escape peaks, and sum peaks in spectra. The degree of line overlap and the best method to account or correct for it must be ascertained on an individual basis and must be considered when calibrating the instrument.

6.2 *Interelement Effects*—Interelement effects, also called matrix effects, exist among all elements as the result of absorption of fluorescent X rays (secondary X rays) by atoms in the specimen. Absorption reduces the apparent sensitivity for the element. In contrast, the atom that absorbs the X rays may in turn emit a fluorescent X ray, increasing the apparent sensitivity for the second element. Mathematical methods may be used to compensate for matrix effects. A number of mathematical correction procedures are commonly utilized including full FP treatments and mathematical models based on influence coefficient algorithms. The influence coefficients may be calculated either from first principles or from the empirical data, or some combination of the two approaches. See Guide E1361 for examples of these approaches. Also, consult the software manual for the spectrometer for information on the approaches provided with the spectrometer. Any of these that will achieve the necessary analytical accuracy is acceptable. Examples of common interelement effects are listed in Table 1.

## 7. Apparatus

7.1 *EDXRF Spectrometer*—Designed for X-ray fluorescence analysis with energy dispersive selection of radiation. The spectrometer is equipped with specimen holders and a specimen chamber. Any EDXRF spectrometer may be used if its design incorporates the following features.

7.1.1 *Source of X-ray Excitation*, capable of exciting the recommended lines listed in Table 2, typically an X-ray tube.

7.1.2 *X-ray Detector*, with sufficient energy resolution to resolve the recommended lines listed in Table 2. An energy resolution of better than 250 eV at Mn K-L<sub>2,3</sub> (K $\alpha$ ) has been found suitable.

**TABLE 1 Common Interelement Effects in Formulated Plastics**

Cause	Effect
Absorption by Cl in PVC	Reduced sensitivity for all analytes as compared to when they are occurring at the same concentration level in polyolefins
Polymers of similar composition but differences in the relative concentrations of H and C	Differences in C/H among calibrants and samples may result in biases of a few percent (relative).
Unmeasured elements B, N, O, and F present in the matrix of the polymer, for example, amide, fluorinated, and terephthalate compounds.	If concentrations differ from the calibrants, substantial concentrations of these elements may cause significant changes in both apparent sensitivity and background count rates.
Absorption by elements present in flame-retardant compounds such as PBBs, PBDEs, and Sb <sub>2</sub> O <sub>3</sub>	Reduction of apparent sensitivity for most analytes
Absorption by Na, P, S, Ca, Ti, Zn, Mo, Sn, Ba, and other elements included in a formulation as fillers or performance additives	Reduction of apparent sensitivity for most analytes

**TABLE 2 Recommended X-ray Lines for Individual Analytes**

NOTE 1—Other choices may provide adequate performance.

Analyte	Preferred Line	Secondary Line
Chromium, Cr	K-L <sub>2,3</sub> (K $\alpha_{1,2}$ )	
Bromine, Br	K-L <sub>2,3</sub> (K $\alpha_{1,2}$ )	K-M <sub>2,3</sub> (K $\beta_{1,3}$ )
Cadmium, Cd	K-L <sub>2,3</sub> (K $\alpha_{1,2}$ )	K-M <sub>2,3</sub> (K $\beta_{1,3}$ )
Mercury, Hg	L <sub>3</sub> -M <sub>4,5</sub> (L $\alpha_{1,2}$ )	
Lead, Pb	L <sub>2</sub> -M <sub>4</sub> (L $\beta_1$ )	L <sub>3</sub> -M <sub>4,5</sub> (L $\alpha_{1,2}$ )

7.1.3 *Signal Conditioning and Data Handling Electronics* that 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 *Secondary Targets*—Used to produce semi-monochromatic radiation enhancing sensitivity for selected X-ray lines and to reduce spectral background for improved detection limits. The use of monochromatic radiation also allows the simplification of FP calculations.

7.2.3 *Specimen Spinner*—Used to reduce the effect of surface irregularities of the specimen.

7.2.4 *Vacuum Pump*—For improved sensitivity of atomic numbers 20 (Ca) or lower, the X-ray optical path may be evacuated using a mechanical pump.

7.2.5 *Helium Flush*—For improved sensitivity of atomic numbers 20 (Ca) or lower, the X-ray optical path may be flushed with helium.

7.3 *Drift Correction Monitor(s)*—Due to 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 [Note 1].

NOTE 1—Suitable drift correction monitors may be fused bead specimens containing the relevant elements (Cr, Br, Cd, Hg, and Pb) or elements that have fluorescence with the same energies as the elements of interest.

## 8. Reagents and Materials

8.1 *Purity of Reagents*<sup>3</sup>—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents used include all materials used for the preparation of reference materials and for cleaning of specimens.

### 8.2 Reagents:

8.2.1 Isopropanol or ethanol.

8.2.2 Nitric acid (HNO<sub>3</sub>).

8.2.3 Hexane.

8.2.4 Deionized water (H<sub>2</sub>O).

8.3 *Gloves*—Disposable cotton gloves are recommended for handling reference materials and other specimens to minimize contamination.

8.4 Appropriate personal protective equipment for the handling of reagents.

### 8.5 Reference Materials:

8.5.1 Polymer reference materials are available from both metrology institutes and commercial sources. Some are provided in disk form, and some are available as granules or extruded pellets.

8.5.2 Reference materials may be prepared by adding known amounts of pure compounds or additives (or both), to an appropriate polymeric base material. It is recommended to make reference materials using the same base polymer as the unknown samples.

8.5.2.1 Thorough mixing of ingredients is required for optimum homogeneity. Options may include grinding, melt-blending, repeated extrusion, and solvent dissolution.

8.5.2.2 Elemental concentrations may be calculated from the concentrations and molecular formulae of the compounds and additives used.

8.5.2.3 The elemental compositions of user-prepared reference materials must be confirmed by one or more independent analytical methods.

### 8.6 Quality Control Samples:

8.6.1 To ensure the quality of the results, analyze quality control (QC) samples at the beginning and at the end of each batch of specimens or after a fixed number of specimens, but at least once each day of operation. If possible, the QC sample shall be representative of samples typically analyzed. The material shall be homogeneous and stable under the anticipated

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annular Standards for Laboratory Chemicals*, BDH Ltd. Poole, Dorset, UK, and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeia Convention, Inc. (USPC), Rockville, MD.

storage conditions. An ample supply of QC sample material shall be available for the intended period of use.

## 9. Hazards

9.1 Occupational Health and Safety standards for X rays and ionizing radiation shall be observed. It is also recommended that proper practices be followed as presented by most manufacturers' documentation. Guidelines for safe operating procedures are also given in current handbooks and publications from original equipment manufacturers. For more information see similar handbooks on radiation safety.

9.2 **Warning**—Appropriate precautions are recommended when working with the elements and compounds of chromium, bromine, cadmium, mercury, and lead in creating polymer mixtures and fused beads.

## 10. Specimen Preparation

10.1 From the polymer to be tested, obtain a flat, smooth piece that is large enough to cover the viewed area of the spectrometer [Note 2]. Specimens shall have no obvious voids within the measured area. It is preferable that the test specimen be either of infinite thickness [Note 3] or the same thickness as the reference materials. The minimum recommended thickness is 2 mm (0.08 in.) [Note 4].

10.1.1 Specimens taken directly from molded components of a product may be analyzed without modification provided their geometry and surface characteristics are suitable. Excessive curvature or rough surface texture will affect the results of the analysis.

10.1.2 *Compression or Injection Molding*—Specimens may be compression molded from pellets, granules or powder. General guidelines for molding may be found in Practice D4703 for compression molding and Practice D3641 for injection molding. Specific conditions for molding specimens may be obtained from the appropriate material specification, if one is available, material supplier's recommendation, or past experience. Select conditions to produce a smooth, plane surface without voids. Since the specimens will not be used for mechanical testing, cooling and heating rates specified for some materials, are not critical.

10.1.3 Specimens may be obtained from sheets of material by cutting, punching, or die cutting. When analyzing thin films and foils, it is acceptable to stack layers of films of the same composition to generate the required thickness. Care must be taken to ensure that the layers are in full contact across the viewed area in the spectrometer and that no air is trapped between layers.

10.1.4 Specimens shall not have surface coatings, nor shall they be attached to a substrate, if the specimen is less than infinitely thick with respect to the X rays of the primary beam, that is, from the X-ray source.

10.2 Prior to measurement, samples of polymers must be cleaned by rinsing with appropriate solvents [Note 5]. In general, non-solvents for the polymer under investigation are appropriate. The following cleaning agents may be used.

10.2.1 Isopropanol or ethanol for removal of non-polar contaminants/hydrophobic (for example, grease).

10.2.2 A solution of 5 % HNO<sub>3</sub> in deionized water for removal of polar/hydrophilic contaminants (for example, salts and most mould release agents).

10.2.3 Hexane for cleaning of polyamide and polyester specimens.

10.3 Care shall be taken to handle the specimen in such a way that oils and salts from the skin do not contaminate the portions of the specimen that will be placed in the X-ray beam path of the spectrometer. The use of disposable cotton gloves is recommended.

NOTE 2—Refer to Appendix XI for alternative specimen handling techniques.

NOTE 3—Materials with a matrix of low atomic number elements, such as polymeric materials, exhibit relatively low X-ray absorption. This leads to a requirement that the specimens must be thick, generally in excess of several millimeters, depending on the X-ray energies to be measured and the composition of the matrix. A minor contribution to the effect comes from the geometry of the instrument used. A specimen thickness of 2 mm is commonly used; however, some laboratories employ lesser or greater thickness (for example, 6 mm to more closely approach infinite thickness). The convenience of making discs of the same thickness for all specimens, instead of infinite thickness, may be a factor for user consideration. In general, more accurate and precise results may be obtained when the reference materials and the unknowns are of infinite thickness or of the same thickness.

NOTE 4—Variations of 10 % relative in thickness at a level of 2 mm have been observed to result in count rate differences of 5 to 10 %. In some cases the effects on the results caused by the variations in thickness may be corrected for by the instrument manufacturer's software or by the calibration, or both.

NOTE 5—Cleaning of reference materials may invalidate the certification. The user is cautioned to consult the certificate of analysis or contact the provider of the reference material for instructions.

## 11. Preparation of Apparatus

11.1 Allow the XRF instrument to stabilize for operation according to the manufacturer's guidelines.

11.2 Follow the manufacturer's recommendations [Note 6] and set up measurement conditions (X-ray tube excitation voltage, tube current, filters, etc.) to measure the count rates of the preferred lines of chromium, bromine, cadmium, mercury, and lead as suggested in Table 2.

11.3 If applicable, measure the Compton scatter radiation resulting from scatter of X-ray tube characteristic lines from the samples [Note 7].

11.4 Calculate a minimum measurement time resulting in a maximum counting statistical error (%CSE) of less than 5 % for a specimen containing approximately 100 mg/kg of the analyte. The required counting time may be calculated by using Eq 1:

$$\% \text{CSE} = 100 / \sqrt{(R \cdot t)} \quad (1)$$

where:

$R$  = net count rate (in counts per second), and

$t$  = counting time in seconds.

11.4.1 The product of  $R$  and  $t$  equals the area under the peak in EDXRF measurements. This time corresponds to a measuring time which results in collection of more than 400 counts (net). Overall measurement time shall not exceed 20 min per specimen [Note 8].