Designation: ~~D6247 – 10~~ D6247 – 18

Standard Test Method for
Determination of Elemental Content of Polyolefins by Wavelength Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D6247; 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~~ Scope*

1.1 This test method covers a general procedure for the determination of elemental content in polyolefins by wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry, in mass fraction ranges typical of those contributed by additives, catalysts, and reactor processes. The elements covered by this test method include fluorine, sodium, magnesium, aluminum, silicon, phosphorus, sulfur, calcium, titanium, chromium, and zinc in the composition ranges given in Table 1.

TABLE 1 Mass Fraction Ranges for Additive and Trace Elements in Polyolefins

Element	Lower Limit (mg/kg)	Upper Limit (mg/kg)
Fluorine	100	300
Sodium	25	200
Magnesium	10	600
Aluminum	40	500
Silicon	30	1000
Phosphorus	5	200
Sulfur	20	200
Calcium	10	300
Titanium	5	200
Chromium	5	100
Zinc	10	1000

1.1.1 This test method does not apply to polymers specifically formulated to contain flame retardants including brominated compounds and antimony trioxide.

1.1.2 This test method does not apply to polymers formulated to contain high levels of compounds of vanadium, molybdenum, cadmium, tin, barium, lead, and mercury because the performance ~~may~~can be strongly influenced by spectral interferences or interelement effects due to these elements.

NOTE 1—Specific methods and capabilities of users may vary with differences in interelement effects and sensitivities, instrumentation and applications software, and practices between laboratories. Development and use of test procedures to measure particular elements, mass fraction ranges or matrices is the responsibility of individual users.

NOTE 2—One general method is outlined herein; alternative analytical practices can be followed, and are attached in notes, where appropriate.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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~~ *safety, health, and* ~~health~~*environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 10.

NOTE 3—There is no known ISO equivalent to this standard.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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*A Summary of Changes section appears at the end of this standard

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems (Withdrawn 2011)[3]

D883 Terminology Relating to Plastics

D4703 Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets

D6247 Test Method for Determination of Elemental Content of Polyolefins by Wavelength Dispersive X-ray Fluorescence Spectrometry

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

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

2.2 *Other Documents:*

JCGM 100:2008 Guide to the Expression of Uncertainty in Measurements

3. Terminology

3.1 *Definitions:*

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

3.2 *Definitions of Terms Specific to This Standard:*

~~3.2.1 *element*—used in this context, refers to any chemical element that can be determined by XRF; and is often used synonymously with the term metal.~~

3.2.1 *infinite thickness*—or critical thickness: the thickness of specimen which, if increased, yields no increase in count rate of secondary (fluorescent) X-rays. This thickness varies with secondary X-ray energy or wavelength.

3.2.2 *polyolefin*—used in this context, refers to polyethylene (PE) and polypropylene (PP) thermoplastics.

4. Summary of Test Method

4.1 The test specimen is compression molded or injection molded into a plaque having a clean, uniform surface.

4.2 The plaque is irradiated in the WDXRF spectrometer with a beam of primary X-rays that causes each element to fluoresce at specific wavelengths (lines). Choices of appropriate lines and spectrometer test conditions can vary according to each element, and with factors such as detector response, mass fraction range, and other elements present in the sample matrix.

4.3 The secondary X-rays are dispersed by crystals and multilayer structures of appropriate spacing, and measured by appropriate detectors configured at angles specific to lines of interest. Additional considerations appear in Guides C1118 and E1621.

4.4 Analyte mass fraction is determined by relation/comparison of measured count rate with a calibration curve.

NOTE 4—An alternative method utilizes a fundamental parameters type calibration.

5. Significance and Use

5.1 Elemental analysis serves as a quality control measure for post-reactor studies, for additive levels in formulated resins, and for finished products. X-ray fluorescence spectrometry is an accurate and relatively fast method to determine mass fractions of multiple elements in polyethylene and polypropylene materials.

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~~ X-rays by the specimen. Overlaps among X-ray lines from elements in the specimen are caused by the limited resolution of the detection subsystem. 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.

6.1.1 The measurement of sodium as an analyte must include correction for the line overlap of zinc L-series lines on sodium K-L$_{2,3}$.

6.1.2 The measurement of fluorine as an analyte must include correction for the overlap of magnesium K-series lines on background measurement angles near the fluorine K-L$_{2,3}$ peak.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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)~~ X-rays (secondary X-rays) by atoms in the specimen and the subsequent fluorescence of a fraction of those atoms. Three options exist for dealing with interelement effects.

6.2.1 *Mathematical Methods*—A number of methods are commonly utilized including full fundamental parameters (FP) treatments and mathematical models based on influence coefficient algorithms. The influence coefficients are calculated either from first principles, 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 2.

6.2.2 *Internal Standard or Internal Reference*—This approach involves the correction of interelement effects by normalizing the measured count rate of an element to the measured count rate of an internal standard element or an internal reference line from the spectrometer.

6.2.2.1 An internal standard element must be chosen carefully and must be added during sample preparation to all specimens in a completely homogeneous manner. The chosen line from the internal standard element can be used for any analyte as long as there are no absorption edges of major constituent elements between the measured line of the analyte and the measured line of the internal standard element.

6.2.2.2 An internal reference line is a peak produced by scattering of primary ~~X rays~~ X-rays from the tube source from the specimen into the monochromator. In most cases, it is appropriate to use the Compton scatter peak, if available. The internal reference line can be used for any analyte as long as there are no absorption edges of major constituent elements between the measured line of the analyte and the internal reference line.

6.2.3 *Restricted Calibration Range*—In this option, the analyst chooses to restrict the maximum mass fractions of the analytes to values below which there are no significant biases due to absorption. The analyst must demonstrate by experiment that interelement effects have been controlled completely.

NOTE 5—Differences in specimen thickness may be a source of bias when the energy of the measured X-ray line is high. Internal standard and internal reference procedures can be used to correct for the effects of these differences. See Section 13.

NOTE 6—The background count rate near the peak of interest can serve as an internal reference measurement in the same way as a peak from scattered primary radiation.

7. Apparatus

7.1 *Calibration Standards Formulation:*

7.1.1 *Batch Compounding Equipment,* with temperature regulation capabilities, for melt homogenization of elemental compounds or additives into polyolefin reference standards. Equipment can range from small scale torque rheometers equipped with mixing head, to large-scale batch mixers. Nitrogen purge capabilities are recommended.

NOTE 7—An alternative method utilizes a single-screw or twin-screw laboratory-scale extruder in place of the melt-fusion head, however, more material is required for formulation. Dry homogenization techniques that do not require the use of melt-compounding apparatus have been used; however, such are not recommended.

7.1.2 *Analytical Balance,* 0.1-mg sensitivity

7.2 *Specimen Preparation:*

7.2.1 *Thermal Press,* for compression-molding of plaques, and capable of obtaining temperatures, pressures and cooling rates, as recommended for PE and PP in Practice D4703 and in Section 11 of this test method.

7.2.2 *Flash Type Mold,* picture-frame type, described in Practice D4703: stainless-steel chase to mold test plaques, uncoated polyester film parting sheets, and smooth, stainless steel backing plates of minimum 2.5 mm thickness.

NOTE 8—Injection molding apparatus have also been employed, in place of the thermal press and flash mold.

NOTE 9—One laboratory has prepared plaques using ~~standard,~~ standard steel dies (designed for preparing briquettes of powder materials) in a hydraulic press. Aluminum pressing caps served as molds. The loaded die was heated in an oven for ≥2 h prior to pressing. During pressing, a laboratory vacuum was drawn on the side port of the die. In the press, the pressure was rapidly increased to 12 tons and the die was allowed to cool to room temperature. The pressing cap was removed from the cooled plaque.

TABLE 2 Common Interelement Effects in Formulated Plastics

Cause	Effect
Polymers of similar composition but differences in the relative mass fractions of hydrogen and carbon.	Differences in C/H among calibrants and samples can result in biases of a few percent (relative).
Unmeasured elements boron, nitrogen, oxygen, and fluorine present in the matrix of the polymer, for example, amide, fluorinated, and terephthalate compounds.	If mass fractions differ significantly from the calibrants, these elements cause significant changes in both apparent sensitivity and background count rates.
Absorption by elements in the scope of the standard or unknown levels of elements outside the scope of the standard (for example, molybdenum, cadmium, tin, and barium) included in the formulation.	Reduction of apparent sensitivity for most analytes.

7.3 *Spectrometer*—Requirements for a wavelength-dispersive XRF spectrometer are outlined in Guides C1118 and E1621.

7.3.1 *Source of X-ray Excitation,* capable of exciting the recommended lines listed in Table 3, typically an X-ray tube.

7.3.2 *X-ray Detectors,* with sufficient sensitivity to detect the recommended lines listed in Table 3. Typical spectrometers include proportional counters, sealed or flow designs, and a scintillation counter.

7.3.3 *Signal ~~conditioning and data handling electronics~~Conditioning and Data Handling Electronics* that include the functions of X-ray counting and peak processing.

7.3.4 *Vacuum Pump*—The X-ray optical path must be evacuated using a mechanical pump.

7.3.5 The following spectrometer features and accessories are optional.

7.3.5.1 *Beam Filters*—Used on the primary X-ray beam to make the excitation more selective and to reduce background count rates.

7.3.5.2 *Specimen Spinner*—Use is recommended to reduce the effect of surface irregularities of the specimen.

7.4 *Drift Correction Monitor(s)*—Due to instability of the measurement system, the sensitivity and background of the spectrometer ~~may~~will drift with time. Drift correction monitors ~~may~~can 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.~~X-rays.

NOTE 10—Suitable drift correction monitors can be fused bead specimens containing the relevant elements or elements that have fluorescence with the same energies as the elements of interest. It is recommended that monitors provide count rates near to the low and high ends of the ranges typically encountered from plastic specimens.

7.5 *Gloves*—Disposable cotton gloves are recommended for handling all specimens to minimize contamination.

7.6 *Personal Protective Equipment*—Appropriate personal protective equipment for the handling of reagents and hot equipment.

8. Reagents and Materials

8.1 *P-10 Gas,* a mixture of 90 % argon and 10 % methane, ultra-high purity or equivalent, for use with gas-flow proportional detectors.

NOTE 11—Some instrument manufacturers allow the use of P-5 gas (95 % argon and 5 % methane).

8.2 *Nitrogen,* prepurified grade or equivalent, for purging the melt fusion chamber.

8.3 *Elemental Standards*—Compounds or additives, or both, to be ~~melt homogenized~~melt-homogenized into polymer calibration standards. Materials must have reliable elemental assays or known stoichiometry prior to use.

NOTE 12—One laboratory has prepared polymer calibration standards by dissolving organometallic compounds in xylenes and adding known amounts to low density polyethylene dissolved in xylenes in TFE-flurocarbon beakers at 100°C with stirring. After removal of the solvents, the solids were ground in an ultracentrifugal mill and melt pressed.

9. Reference Materials

9.1 Users can prepare reference materials in house. A technique that offers consistent elemental dispersion throughout the calibration standard must be followed. Melt homogenization to ensure uniformity is recommended; see Annex A1.

NOTE 13—Resins from actual production runs have been used for calibration standards, after value assignment by independent analytical methods.
NOTE 14—One laboratory has successfully used glass reference materials and fundamental parameters-based calibrations. Another laboratory has successfully used oil-based reference materials to calibrate a method.

9.2 Certified reference materials are available from national metrology institutes and commercial suppliers.

10. Safety Precautions

10.1 *Occupational Health and Safety Standards for X-rays,* and ionizing radiation shall be observed. It is also recommended that proper practices be followed, as shown in Guide E1621.

TABLE 3 Recommended X-ray Lines for Individual Analytes

Analyte	Preferred Line	Alternate Line
~~Fluorine~~	~~K-L$_{2,3}$ (K$\alpha_{1,2}$)~~	
Fluorine, F	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Sodium, Na	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
~~Magnesium~~	~~K-L$_{2,3}$ (K$\alpha_{1,2}$)~~	
Magnesium, Mg	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
~~Aluminum~~	~~K-L$_{2,3}$ (K$\alpha_{1,2}$)~~	
Aluminum, Al	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Silicon, Si	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Phosphorus, P	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Sulfur, S	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Calcium, Ca	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Titanium, Ti	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Chromium, Cr	K-L$_{2,3}$ (K$\alpha_{1,2}$)	
Zinc, Zn	K-L$_{2,3}$ (K$\alpha_{1,2}$)	K-M$_{2,3}$ (K$\beta_{1,3}$)

NOTE 15—X rays X-rays are dangerous and can cause serious personal injury. X-ray beams can be very narrow and difficult to detect. Precautions taken minimize potential radiation exposure include an increase in protective shielding, an increase of distance, and a decrease of time near any suspected source of leakage. Modern commercial spectrometers typically have the appropriate shielding and safety interlocks. Monitoring equipment may be required by local safety codes. It is possible that local safety codes or regulations demand monitoring equipment; and/or regular safety checks. Refer to 1.3.

10.2 *Chemical*—Appropriate precautions for chemical hazards shall be observed for any chemicals and materials used in preparing calibration standards. Consult the suppliers' Material Safety Data Sheets for specific hazards and safety practices.

10.3 *Pressurized Gas Gas*— requiresRequires safe and proper handling practices.

10.4 *Specimen Preparation*—Follow appropriate precautions when using hot equipment for homogenization and specimen preparation. Consult the manufacturer's recommendations for specific practices.

11. Preparation of Reference Materials and Test Specimens

11.1 *Specimen Plaques*—Consistent preparation of reference materials and test specimens is essential. Variations in sample thickness, surface finish and homogeneity can affect reliability of results.

11.1.1 *Test Specimens*—The level of heterogeneity of an element in a specimen may not be known. For most of the elements in this standard, heterogeneity is a potential source of bias. A potential source of bias is introduced when one or more elements are not distributed homogeneously throughout the specimen. This cannot be corrected for. See Annex A1 for procedures designed to reduce heterogeneity.

11.2 *Compression Molding*—Both calibration standards and test specimens are pressed into plaques. The laboratory must choose a thickness and use it consistently. Each plaque shall have a smooth, plane surface, and no voids. Refer to Practice D4703. If the resulting plaque is too large in diameter to fit the instrument, cut or punch a piece of the correct diameter.

NOTE 16—Use of a laboratory-scale injection molding technique is an acceptable alternative to the compression molding method.
NOTE 17—Laboratories and manufacturers of reference materials employ plaques having different thickness. Thinner specimens will be less than infinitely thick for zinc X rays, X-rays, and if <2 mm thick, may bethey are less than infinitely thick for chromium X rays. X-rays. It is recommended to employ a narrow range of thickness for optimum method performance.

11.2.1 Weigh the required mass of plastic and place into the compression or molding apparatus.

11.2.2 Place the assembly into the press or oven, which has been preheated. Compress the sample under appropriate pressure and time settings to obtain a suitable specimen plaque.

NOTE 18—Appropriate temperatures vary depending on the apparatus. For example, thermal presses and flash molds are set to 175°C for PE and 200°C for PP. For steel briquette dies, temperatures of 140°C for PE and 185°C for PP have been used successfully.

11.3 *Cooling Rate* is chosen to yield a uniform, smooth plaque.

11.3.1 *Programmed Cooling*—After a pre-programmed dwell time at high pressure, initiate cooling at a recommended rate of 15 ± 2°C per minute,

11.3.2 *Quick Cooling*—Remove the hot assembly and pressurize in a water-cooled press, or equivalent, and allow it to cool to ambient temperature, or

11.3.3 *Slow Cooling*—When using a steel briquette die, allow the die to cool undisturbed in the hydraulic press to room temperature.

11.4 It is recommended to clean specimen surfaces with isopropyl alcohol (or methyl alcohol);or ethyl alcohol, immediately prior to measurement. Operator experience may show this need to vary with the element or additive to be measured.The need for this cleaning varies with the elements and/or the additives to be measured, as well as the specimen preparation and specimen handling. Experience gained during the routine application of this standard test method provides good guidance in this respect.

11.4.1 Care shall be taken to handle only the sides, not the surfaces of the specimen following molding or cleaning so that oils and salts from the skin do not contaminate the specimen. Disposable cotton gloves may be wornThe use of disposable cotton gloves when handling specimens to prevent reduces the risk of inadvertent contamination.

12. Preparation of Apparatus

12.1 A description of considerations is included in Guide E1621.

12.2 Allow the WDXRF spectrometer to stabilize for operation according to the manufacturer's guidelines or the laboratory operating procedure.

12.3 In a manner consistent with the manufacturer's recommendations, set up measurement conditions (X-ray tube excitation voltage, tube current, filters, goniometer angles, pulse height discrimination, etc.) to measure the count rates of the preferred lines (or alternate lines) of the analytes.

12.3.1 Include subtraction of background for all elements. Measure at least one background point for each element.

12.4 If applicable, include measurement of the Compton scatter radiation resulting from scatter of X-ray tube characteristic lines from the samples.

12.4.1 The use of the background count rate for the element is an alternative to the Compton scatter radiation.

Note 19—Depending on the anode material of the X-ray tube, Compton scatter radiation may ~~or may~~ not be observable. For example, tubes with anodes of Mo, Rh, Ag, Pd (atomic numbers 42 and higher) provide strong Compton scatter radiation. In contrast, tube anodes consisting of chromium and scandium are of little or no use as an internal ~~reference.~~ reference, as they exhibit very little Compton scatter.

12.5 For each analyte, calculate a minimum counting time resulting in a maximum counting statistical error (%CSE) of less than 2 % for a specimen containing approximately 100 mg/kg of the analyte. The required counting time may be calculated by using Eq 1:

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

where:
R = net count rate (in counts per second) and
t = counting time in seconds.

This corresponds to the time necessary to collect more than 2500 counts. Overall measurement time for all analytes shall not exceed 20 min per specimen.

Note 20—Often, the operating system of the spectrometer will include procedures for calculating measurement times. Such procedures typically include background measurement times, if appropriate.

Note 21—Polymer materials are subject to damage by ionizing radiation. Susceptibility to damage varies greatly among common polymers. The user is cautioned to keep measurement times as short as practical and to avoid the repeated measurement of a single specimen. For this reason, it is recommended to use fixed counting times as opposed to fixed total counts, ~~which may~~ as this can result in extraordinary long measurement times for some ~~specimens.~~specimens with low concentrations of one or more analytes.

13. Calibration

13.1 Consideration options are covered in Guide E1621.

13.2 When calibrating, use one of the described calibration methods: an empirical calibration, or a fundamental parameters (FP) calibration. Both methods rely on the use of a set of known standards and/or certified reference materials.

13.3 *Empirical calibration*—Prepare or obtain a set of calibration standards that cover the mass fraction range of interest of each analyte prepared in the matrix of interest including the relevant interferences described in Section 6. 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. As far as practical, ensure that the mass fractions of different analytes in the same set of calibration standards do not vary in proportion to each other among the individual standards. Ensure that the low mass fraction of one analyte is combined with a higher mass fraction of another analyte. It is important to have several standards available for each analyte when using an empirical calibration to provide enough degrees of freedom to determine empirically the influence coefficients as well as the slope and intercept of the calibration curve.

13.3.1 In an empirical approach with a low number of calibration standards, calculate influence coefficients from theory (using FP).

13.3.2 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 12.

13.3.3 Measure each standard at least twice preferably with two ~~separately~~independently prepared specimens.

13.3.4 For each analyte, follow the manufacturer's instructions to perform a regression of net count rate versus mass fraction.

Note 22—Linear calibration curves were found by some laboratories to be suitable for the element mass fractions listed in the scope of this test method.
Note 23—X-ray fluorescence data for calibration is heteroscedastic. This means that calibration regressions that include a weighting scheme that favors low mass fraction calibration standards are recommended. Failure to use a weighting factor could result in bias at the low mass fraction end of the fitted calibration algorithm. Spectrometer regression software typically includes a means for applying linear or square-root weighting plus constant factors.

13.3.4.1 As an option, the net count rates ~~may~~can first be divided by the count rate for the internal standard or internal reference measurement for the specimen.

13.3.4.2 As an option, include corrections for significant interelement effects (see 6.2) in the regression model by using influence coefficients.

13.3.5 Include spectral interferences (peak overlaps) in the regression algorithm.

13.3.5.1 The calibration of sodium must include correction of the line overlap of zinc L-series lines on sodium K $L_{2,3}$.

13.4 *FP Calibration:*

13.4.1 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 must be available. Corrections for interelement effects are done entirely from theory.

13.4.2 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 12.

13.4.3 Measure each standard, if possible at least twice preferably with two separately prepared specimens.

13.4.4 For each analyte, follow the manufacturer's instructions to perform a regression of net count rate versus mass fraction.

13.4.5 If the spectrum processing options do not include corrections for peak overlaps, corrections must 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.

13.4.5.1 The calibration of sodium must include correction ~~of~~for the line overlap ~~of~~by zinc L-series lines on sodium K L$_{2,3}$.

13.4.6 FP methods often require the sum of calculated constituents of a sample to be 100 %. Typically, results are improved when the matrix of the specimen is modeled as a compound of hydrogen, carbon, nitrogen, and oxygen approximating the actual polymer composition.

13.4.7 As an option, the inclusion of the count rate of Compton scattered radiation (or Compton/Rayleigh scattered radiation ratio) in the FP algorithm ~~may~~can be used to compensate for matrix effects caused by sample elements that cannot be measured directly.

14. Procedure

14.1 Load the prepared specimen plaque into the spectrometer using the appropriate accessories.

14.2 Measure the specimen using the conditions chosen in Section 12 and record the count rates.

14.3 Calculate the mass fractions of the analytes using the calibrations implemented in Section 13.

15. Reporting Results

15.1 Report the following information:

15.1.1 Unique identification of the sample. This ~~may vary~~ identification system varies according to laboratory procedures and test purposes.

15.1.2 The date and time of the test.

15.1.3 The results of this test expressed to the nearest 0.1 mg/kg for mass fractions <50 mg/kg and to the nearest 1 mg/kg for higher mass fractions. Follow the relevant procedures in Practice E29.

15.1.4 A reference to this standard method of test (D6247).

15.1.5 The origin of the sample.

15.1.6 Deviations from this standard, if any.

16. Precision and Bias[4]

16.1 *Precision*—Eighteen laboratories cooperated in testing this method and obtaining the information summarized in Tables 4-14. The cooperative testing was conducted and the data was analyzed in accordance with Practice E1601, Test Plan A. The materials provided for the test were evaluated prior to the study and found to be characterized by levels of heterogeneity negligible in comparison to the components of variance calculated using Practice E1601.

16.1.1 In Tables 4-14, the information for test materials having fewer than six laboratories does not comply with Practice E1601. There is wide agreement that estimates of precision based upon fewer than six laboratories become increasingly unreliable as the number decreases. The information is given for the purpose of completely specifying the conditions under which the scope of this test method was developed.

16.2 *Bias*—A number of certified reference materials were tested in the development of this test method. The accuracy of this test method has been deemed satisfactory based on the bias data in Tables 4-14. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

16.2.1 The certified values listed in Tables 4-14 are actually a mix of certified values, reference values, and information values. It is important to refer to the certificates of analysis to obtain the actual values, their uncertainty estimates, and their assignment categories.

NOTE 24—Procedures for testing for bias between measured results and assigned (certified) values are beyond the scope of this standard. Information and examples can be found in NIST Special Publication 829. Discussion and procedures for interpretation of uncertainty estimates for assigned values can be found in the certificate of analysis of the reference material and in the ISO Guide to the Expression of Uncertainty in ~~Measurements.~~Measurements (JCGM 100:2008).

17. Keywords

17.1 element; polyolefin; X-ray fluorescence spectrometry (XRF)

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1251.

TABLE 4 Fluorine—Statistical Summary

(All values in units of mg/kg)

Test Material	No. Laboratories	Mean	Minimum SD, s_M (E1601)	Reproducibility SD, s_R (E1601)	Reproducibility Index, R (E 1601)	R_{Rel}, %
D	0					
F	3	15.6	4.9	16.6	46.5	297
E	3	46.5	5.6	19.6	54.8	118
H	3	158.1	6.7	36.1	101.0	64
G	3	209.3	11.8	53.3	149.4	71
A	7	13.5	13.5	21.9	61.2	452
B	6	7.6	7.0	20.9	58.6	770
C	6	7.5	22.4	30.6	85.7	1143

Test Material	Certified	Number	Source	Description
D	< 5	ADPOL Blank	PANalytical	Additive Elements in Polyethylene
F	27	ADPOL RM2	PANalytical	Additive Elements in Polyethylene
E	64	ADPOL RM1	PANalytical	Additive Elements in Polyethylene
H	162	ADPOL RM4	PANalytical	Additive Elements in Polyethylene
G	266	ADPOL RM3	PANalytical	Additive Elements in Polyethylene
A	—	SRM 2855, Level I	NIST	Additive Elements in Polyethylene
B	—	SRM 2855, Level II	NIST	Additive Elements in Polyethylene
C	—	SRM 2855, Level III	NIST	Additive Elements in Polyethylene

TABLE 5 Sodium—Statistical Summary

(All values in units of mg/kg)

Test Material	No. Laboratories	Mean	Minimum SD, s_M (E1601)	Reproducibility SD, s_R (E1601)	Reproducibility Index, R (E 1601)	R_{Rel}, %
A	3	3.6	4.6	4.6	12.8	355
D	0					
F	3	16.1	2.5	11.4	31.8	198
B	3	10.8	11.1	12.1	34.0	314
C	0					
E	3	61.1	6.3	16.4	45.9	75
H	3	95.8	8.2	21.6	60.6	63
G	3	176.9	33.5	52.5	147.0	83

Test Material	Certified	Number	Source	Description
A	< 4	SRM 2855, Level I	NIST	Additive Elements in Polyethylene
D	< 0.5	ADPOL Blank	PANalytical	Additive Elements in Polyethylene
F	10.1	ADPOL RM2	PANalytical	Additive Elements in Polyethylene
B	16.0	SRM 2855, Level II	NIST	Additive Elements in Polyethylene
C	16.4	SRM 2855, Level III	NIST	Additive Elements in Polyethylene
E	43	ADPOL RM1	PANalytical	Additive Elements in Polyethylene
H	104	ADPOL RM4	PANalytical	Additive Elements in Polyethylene
G	189	ADPOL RM3	PANalytical	Additive Elements in Polyethylene

TABLE 6 Magnesium—Statistical Summary

(All values in units of mg/kg)

Test Material	No. Laboratories	Mean	Minimum SD, s_M (E1601)	Reproducibility SD, s_R (E1601)	Reproducibility Index, R (E 1601)	R_{Rel}, %
D	3	3.6	1.1	2.0	5.5	156
E	3	26.5	1.6	1.6	4.4	16.6
H	3	98.5	5.0	6.7	18.9	19.1
G	3	237.8	1.3	4.8	13.5	5.7
F	3	561.1	2.0	2.0	5.8	1.0
A	0					
B	0					
C	0					

Test Material	Certified	Number	Source	Description
D	< 1	ADPOL Blank	PANalytical	Additive Elements in Polyethylene
E	28	ADPOL RM1	PANalytical	Additive Elements in Polyethylene
H	102	ADPOL RM4	PANalytical	Additive Elements in Polyethylene
G	248	ADPOL RM3	PANalytical	Additive Elements in Polyethylene
F	561	ADPOL RM2	PANalytical	Additive Elements in Polyethylene
A	—	SRM 2855, Level I	NIST	Additive Elements in Polyethylene
B	—	SRM 2855, Level II	NIST	Additive Elements in Polyethylene
C	—	SRM 2855, Level III	NIST	Additive Elements in Polyethylene