Standard Test Method for
Analysis of Elemental Content in Polyolefins By X-Ray Fluorescence Spectrometry[1]

1. Scope

1.1 This test method covers a general procedure for the determination of elemental content in polyolefins by X-ray fluorescence spectrometry, in concentration levels typical of those contributed by additives and reactor processes.

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, concentration 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. The inch-pound units given in parentheses are for information only.

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

NOTE 3—There is no similar or equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*
C 1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems[2]
D 883 Terminology Relating to Plastics[3]
D 4703 Practice for Compression-Molding Thermoplastic Materials into Test Specimens, Plaques or Sheets[4]
E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[5]
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[6]
E 1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis[7]
E 1621 Guide for X-Ray Emission Spectrometric Analysis[7]

3. Terminology

3.1 *Definitions*:
3.1.1 Definitions of terms applying to XRF and plastics appear in Terminology E 135 and Terminology D 883, 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.

3.2.2 *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. This thickness varies with secondary x-ray energy, or wavelength.

3.2.3 *polyolefin*—used in this context, refers to PE and 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 with a beam of primary X-rays, that causes each element to fluoresce at specific wavelengths (lines). Choice of appropriate lines and spectrometer test conditions can vary according to each element, and with factors such as detector response, concentration range, and other elements present in the sample matrix.

4.3 These secondary X-rays are dispersed with diffraction crystals of appropriate spacing, and measured by appropriate detectors configured at angles specific to lines of interest. Additional considerations appear in Guides C 1118 and E 1621.

4.4 Analyte concentration is determined by relation/comparison of line intensity with a calibration curve.

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

5. Significance and Use

5.1 X-ray fluorescence spectrometry is an accurate and relatively fast method to determine multielement concentrations in polyethylene or polypropylene materials, or both. It can be used as a quality control measure for post-reactor studies, for additive levels in formulated resins, and for finished products.

5.2 Further elaboration appears in Guide E 1621.

6. Interferences

6.1 Potential interferences are explained in Guide E 1621.

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 larger-scale batch mixers. Nitrogen purge capabilities are recommended.

NOTE 5—An alternative method requires 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 which 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 D 4703 and in Section 11 of this test method.

7.2.2 *Flash Type Mold*, picture-frame type, described in Practice D 4703: stainless-steel chase to mold test plaques 3.2 mm (0.125 in.) thick, uncoated Mylar[8] (polyester film) parting sheets, and smooth, stainless steel backing plates of minimum 2.5 mm thickness.

NOTE 6—Injection molding apparatus have also been employed, in place of the thermal press and flash mold.

NOTE 7—The recommended thickness of 3.2 mm may vary with user preference. Other material may be used for parting sheets, provided it does not adhere to the polymer under such thermal conditions. Some techniques use polished steel backing plates, with chromed surfaces, and no parting sheets. The apparatus used should not introduce contamination of elements of interest, and should yield specimens with a plane surface of adequate smoothness.

7.3 *Excitation Source, Spectrometer, and Measuring System*—Requirements for a wavelength-dispersive XRF are outlined in Guides C 1118 and E 1621.

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.

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 into polymer calibration standards. Material should be certified as to elemental purity and should be dried and desiccated prior to use.

9. Reference Materials

9.1 *Reference Materials*, can be prepared by users, as in Section 11.

9.2 *Other Materials*, appear in Guide E 1621.

9.3 *Monitor Samples*—To account for instrument drift (for example, electronic variations or long term X-ray source degradation).

NOTE 8—Monitor samples are selected for their long-term durability, and should ideally contain elements near to high and low ends of analytical range(s) of interest. Prefabricated glass discs outside range(s) of interest are often used. They are measured before measurement of calibration standards, and are remeasured periodically (for example, daily). Any drift from original measurements can be accounted for, and necessary corrections can be applied to maintain calibrations relative to initial conditions.

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 E 1621.

NOTE 9—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.

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* requires safe and proper handling practices.

10.4 *Specimen Preparation*—Follow appropriate precautions when using hot equipment for homogenization and specimen preparation. Consult 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 *Reference Materials*—A technique that offers consistent elemental dispersion throughout the calibration standard should be followed. Melt homogenization to ensure uniformity is recommended; see Annex A1.

NOTE 10—Resins from actual production runs have been used for calibration standards, after verification by independent analytical methods.

11.1.2 *Test Specimens*—If elemental dispersion is poor, homogenize the sample according to Annex A1, Section 2. If elemental dispersion is acceptable, proceed to 11.2.

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[8] Mylar is a registered trademark of DuPont.

11.2 *Compression Molding*—Both calibration standards and test specimens are pressed into plaques having a suggested thickness of 3.2 mm (0.125 in.). Each plaque should have a smooth, plane surface, and no voids. Refer to Practice D 4703.

NOTE 11—Techniques using no polymer-based calibration have been used.

NOTE 12—Some users employ a laboratory-scale injection molding technique as an alternative to this suggested compression molding method.

NOTE 13—A thickness of 3.2 mm is commonly used, however, some laboratories employ lesser or greater thicknesses (for example, 6 mm, to more closely approach infinite thickness; or extruded thin films and sheets). The convenience of making a plaque of one thickness for all elements, versus infinite thickness may be a factor for user consideration.

NOTE 14—Plaques may be molded in the proper dimensions to fit the instrument, or may be of a larger size, from which the specimen plaque is punched out.

11.2.1 Weigh the required mass of plastic and place into the hollow chase of the picture frame flash mold assembly, which is sandwiched between Mylar[8] parting sheets, and supported by smooth backing plates.

11.2.2 Place the assembly into the press, which has been preheated to 175°C for PE and 200°C for PP. Heat the sample under appropriate pressure and time settings to obtain a suitable specimen plaque.

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

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, or:

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.

11.4 It is recommended to clean specimen surfaces with isopropyl alcohol (or methyl alcohol), immediately prior to measurement. Operator experience may show this need to vary with the element or additive to be measured.

11.4.1 Care should be taken to handle only the sides, not the surface 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 worn when handling specimens to prevent inadvertent contamination.

12. Preparation of Apparatus

12.1 A description of considerations is included in Guide E 1621.

NOTE 15—Measurement of Kα lines is recommended, where possible.
NOTE 16—A reduction of X-ray tube power used (for example -10 % current) can result in an overall increase in tube life.

13. Calibration and Standardization

13.1 Considerations are covered in Guide E 1621.

NOTE 17—Background subtraction is a suggested correction method for polyolefins. A linear calibration curve was suitable for the elemental concentrations listed in the annex. Higher concentrations may require mathematical corrections covered in Guide E 1361.

NOTE 18—One alternative calibration method, using fundamental parameters software, required measurements of only one polymer blank and one standard per element (for example, 0.5 % analyte element in mineral oil).

14. Procedure

14.1 Refer to Guide E 1621.

NOTE 19—The effects of poor surface finish on test accuracy can become more adverse at longer wavelengths (lower atomic numbers) and at lower analyte concentrations. The use of a sample spinner is recommended.

14.2 It is recommended to measure monitor sample(s) daily, for elements of interest, and to apply any required drift corrections to sample measurements.

14.3 Participating laboratories preferred a fixed counting time over a fixed number of counts.

15. Interpretation of Results

15.1 Refer to Guide E 1621.

16. Precision and Bias

16.1 *Instrument Repeatability*—Repeatability of one instrument in one laboratory measuring one single specimen of an experimental formulation 30 times is shown in Table 1.

16.2 *Round Robin Study*:

16.2.1 Precision and bias statements are currently under evaluation. Data were obtained in a round robin study conducted in 1992, in accordance with Practice E 691, involving two groups of commercial grade materials (one group of polyethylene, one group of polypropylene), with each group containing three materials (that is a total of six materials). The grades were selected on the basis of their relative elemental content levels, from low (< 10 ppm), to medium (< 200 ppm), to high (> 200 and< 5000 ppm); as contributed by catalyst residues or additives. Each grade was relatively free of interferences and interelemental effects. Reference values for the elements selected for testing in each of the round robin samples were determined by neutron activation analysis.

16.2.2 To minimize variations in elemental dispersion, each sample material was homogenized by triple extrusion passes. Polyethylene and polypropylene sample groups were prepared by each of two laboratories respectively, and distributed to each round robin participant under cover of these respective labs. Twelve laboratories participated in this study. Each round robin participant had the option to analyze either one, or both groups of materials. The polyethylene sample group was tested for a total of nine elements; the polypropylene sample group was tested for a total of eight elements. Each sample was tested for a specified set of elements selected from within its respective group.

16.2.3 Each sample was analyzed in duplicate on each of three separate days (that is a total of six determinations per sample, of each specified element). Each laboratory conducted measurements only on elements it analyzed for on a routine basis. All testing was conducted on WDXRF instruments.

TABLE 1 Instrument Repeatability

Element	Mean Concentration (ppm)	Standard Deviation
P	18.9	0.20
Si	1538	3.4
Zn	58.1	0.22

16.3 The following explanations of *r* and *R* (16.4-16.4.3 are intended to present a meaningful way of considering the approximate precision of this test method, as applicable to each respective element reported, and at the concentration levels outlined in Table 2. The data under evaluation should not be applied rigorously to acceptance or rejection of a material, as those data are specific to the round robin, and may not be representative of other lots, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 16.4-16.4.3 would then be valid for such data.

TABLE 2 Referee Elemental Concentrations as Determined by Neutron Activation Analysis[A]

Element	Metal PE1	Metal PE2	Metal PE3	Metal PP1	Metal PP2	Metal PP3
Al	134	2.9	116	80	62	29
Ca	...	...	100	...	25	45
Cr	...	1.16	...	...	...	...
Fe	33 ± 4	...	...	...	...	...
Mg	12 ± 2	...	23 ± 3	13 ± 2	...	...
P	...	90	74	69	36	...
Si	1503	206 ± 20	3338	827	349	...
S	...	...	...	...	< 85	64 ± 20
Ti	5.3	...	7.7	2.5	2.2	0.74
Zn	...	63	...	199	...	...

[A]Precision ± 5 %.

16.4 *Concept of r and R*—If S_r and S_R have been calculated from a large enough body of data, and for test results that were averages from testing six specimens, the following applies:

16.4.1 *Repeatability Limit, r (Comparing Two Test Results for the Same Material, Obtained by the Same Operator Using the Same Equipment on the Same Day)*—The two test results should be judged not equivalent if they differ by more than the *r* value for that material.

16.4.2 *Reproducibility Limit, R (Comparing Two Test Results for the Same Material, Obtained by Different Operators in Different Laboratories)*—The two test results should be judged not equivalent if they differ by more than *R* value for that material.

16.4.3 Any judgement in accordance with 16.4.1 or 16.4.2 would have an approximate 95 % (0.95) probability of being correct.

16.5 *Bias (Accuracy)*—Capabilities of individual laboratories resulted in differing numbers of participants contributing to measured data, depending upon each particular element, and its concentration. Table 2 shows referee concentrations, as determined by neutron activation analysis.

17. Keywords

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

ANNEX

(Mandatory Information)

A1. PREPARATION AND MELT HOMOGENATION OF SPECIMENS

A1.1 *Preparation of Reference Standards*—Accurately weigh appropriate quantities of respective additives/compounds into the dried, granular polymer.

A1.2 *Melt Homogenization* is used to minimize local variations of additive/element concentration. Batch compounding equipment is recommended to ensure accurate mass balance(s) throughout the mixing process. A torque rheometer equipped with mixing head, or a larger melt compounder is suitable.

Note A1.1—Although batch compounding is recommended, some users melt-homogenize via single or multiple passes of the polyolefin standard through a laboratory-scale extruder.

Note A1.2—Dry homogenization requires less apparatus, but may yield less uniform standards. This technique is not recommended. Elements or additives, or both, are dissolved in appropriate solvents, in specified concentrations. Aliquots of appropriate volumes are distributed evenly into preweighed quantities of additive-free granular resin, in respective evaporating dishes. These are manually stirred while evaporating to dryness on a non-flammable heat source such as a steam bath.

A1.2.1 *Calibration Standards* must be melt homogenized prior to their use as reference materials for calibration.

A1.2.2 *Test Specimens*—Melt homogenization is recommended for test specimens.

A1.2.3 *Antioxidant Stabilization* of sufficient concentration to prevent thermal degradation of base resins during homogenization is required. The antioxidant used should not contain elements which interfere with elemental lines of interest.

A1.2.4 *Blending* should be carried out under conditions suitable to the resin and equipment used. Temperatures 30 to 50°C above resin melt temperatures are recommended. Mixing rate and time are chosen to ensure adequate uniformity and minimal degradation of samples. The use of a nitrogen purge is recommended.

Note A1.3—Purge with nitrogen at a rate which provides an inert nitrogen blanket.

Note A1.4—Operator experience may dictate adjustment of blending conditions for certain immiscible compounds.

A1.2.5 *Cooling*, after mixing, quickly remove samples and cool as rapidly as possible for safety and stability reasons. Some users quench cool in liquid nitrogen or ice water. After sufficient cooling and drying, mold the required quantity into test plaques.