



Designation: D 6247 – 98

Standard Test Method for Analysis of Elemental Content in Polyolefins By X-Ray Fluorescence Spectrometry¹

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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) Systems²
- D 883 Terminology Relating to Plastics³
- D 4703 Practice for Compression-Molding Thermoplastic Materials into Test Specimens, Plaques or Sheets⁴
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁵
- E 691 Practice for Conducting an Interlaboratory Study to

¹ This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods. Current edition approved April 10, 1998. Published February 1999.

² *Annual Book of ASTM Standards*, Vol 12.01.

³ *Annual Book of ASTM Standards*, Vol 08.01.

⁴ *Annual Book of ASTM Standards*, Vol 08.03.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

Determine the Precision of a Test Method⁶

E 1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis⁷

E 1621 Guide for X-Ray Emission Spectrometric Analysis⁷

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.

⁶ *Annual Book of ASTM Standards*, Vol 14.02.

⁷ *Annual Book of ASTM Standards*, Vol 03.06.

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 Mylar⁸ (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.

⁸ Mylar is a registered trademark of DuPont.