



Standard Test Method for Chlorine in Aromatics by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry¹

This standard is issued under the fixed designation D 7536; 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 the determination of chlorine by monochromatic, wavelength-dispersive X-ray fluorescence (MWDXRF) spectrometry in aromatic hydrocarbons, their derivatives, and related chemicals.

1.2 This test method is applicable to samples with chlorine concentrations from 0.5 mg/kg to 15 mg/kg. Higher chlorine concentrations can be determined by quantitatively diluting the sample with a suitable solvent. In a preliminary robustness study, the limit of detection was estimated to be 0.06 mg/kg.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E 29.

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. For specific hazard information, see Section 9.*

2. Referenced Documents

2.1 ASTM Standards:²

D 3437 Practice for Sampling and Handling Liquid Cyclic Products

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D 6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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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.

2.2 Other Documents:³

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Terminology

3.1 See Terminology D 4790 for definitions of terms used in this test method.

4. Summary of Test Method

4.1 A monochromatic X-ray beam with a wavelength suitable to excite the K-shell electrons of chlorine is focused onto a test specimen contained in a sample cell (see Fig. 1). The fluorescent $K\alpha$ radiation at 0.473 nm (4.73Å) emitted by chlorine is collected by a fixed monochromator (analyzer). The intensity (counts per second) of the chlorine X-rays is measured using a suitable detector and converted to the concentration of chlorine (mg/kg) in a test specimen using a calibration equation. Excitation by monochromatic X-rays reduces background, simplifies matrix correction and increases the signal/background ratio compared to polychromatic excitation used in conventional WDXRF techniques.⁴

5. Significance and Use

5.1 This test method provides for the precise measurement of the chlorine content of aromatics with minimal sample preparation and analyst involvement. The typical time for each analysis is five or ten minutes.

5.2 Knowledge of the chlorine content of aromatics is important for process control as well as the prediction and control of operational problems such as unit corrosion and catalyst poisoning, and in the blending of products to commodity specifications.

5.3 Various federal, state, and local agencies regulate the chlorine content of some petroleum products, including aromatics. Unbiased and precise determination of chlorine in aromatics is critical to compliance with regulatory standards.

5.4 When the elemental composition of the samples differ significantly from the calibration standards used to prepare the

³ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

⁴ Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis*, Plenum Press, New York, 1975, pp. 115-118.

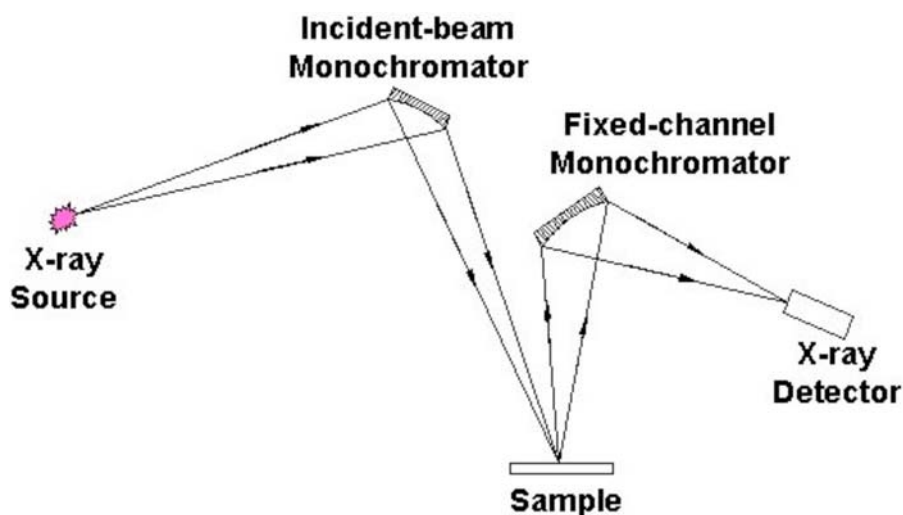


FIG. 1 Schematic of the MWDXRF Analyzer

calibration curve, the cautions and recommendation in Section 6 should be carefully observed.

6. Interferences

6.1 Differences between the elemental composition of test samples and the calibration standards can result in biased chlorine determinations. For aromatics within the scope of this test method, matrix correction can be avoided with a proper choice of calibrants. To minimize any bias in the results, use calibration standards prepared from chlorine-free base materials of the same or similar elemental composition as the test samples.

7. Apparatus

7.1 *Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) Spectrometer*⁵, equipped for X-ray detection at 0.473 nm (4.73Å). Any spectrometer of this type can be used if it includes the following features, and the precision of test results are in accordance with the values described in Section 16.

7.1.1 *X-ray Source*, capable of producing X-rays to excite chlorine. X-ray tubes capable of producing Rh L α , Pd L α , Ag L α , Ti K α , Sc K α , and Cr K α radiation are recommended for this purpose.

7.1.2 *Incident-beam Monochromator*, capable of focusing and selecting a single wavelength of characteristic X-rays from the source onto the specimen.

7.1.3 *Optical Path*, designed to minimize the absorption along the path of the excitation and fluorescent beams using a vacuum or a helium atmosphere. The calibration and test measurements must be done with identical optical paths, including vacuum or helium pressure.

7.1.4 *Monochromator*, suitable for dispersing chlorine K α X-rays.

7.1.5 *Detector*, designed for efficient detection of chlorine K α X-rays.

7.1.6 *Single-Channel Analyzer*, an energy discriminator to monitor only chlorine radiation.

7.2 *Removable Sample Cell*, any specimen holder compatible with the geometry of the MWDXRF spectrometer and designed to use X-ray transparent film (see 7.3) to hold a liquid specimen with a minimum depth of 3 mm. The sample cell must not leak when fitted with X-ray transparent film. A disposable cell is recommended.

7.3 *X-ray Transparent Film*, for containing and supporting the test specimen in the sample cell (see 7.2) while providing a low-absorption window for X-rays to pass to and from the sample. Any film resistant to chemical attack by the sample, free of chlorine, and X-ray transparent may be used.

7.4 *Analytical balance capable of reading to 0.0001 g.*

8. Reagents and Materials

8.1 *Purity of Reagents*—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 where such specifications are available.⁶ 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.

8.2 *Calibration-Check Samples*, for verifying the accuracy of a calibration. The check samples must have known chlorine content and not be used in determining the calibration curve. A standard from the same reliable and consistent source of calibration standards used to determine the calibration curve is convenient to check the calibration.

⁵ The sole source of supply of the apparatus known to the committee at this time is X-Ray Optical Systems, Inc., 15 Tech Valley Drive, East Greenbush, NY, 12061. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annular Standards for Laboratory Chemicals*, BD Ltd., Pole, Dourest, U. K., and the *United States Pharmacopoeia and National Formulary*, U. S. Pharmaceutical Convention, Inc. (SUPT.), Rockville, MD.