Designation: ~~D7536 – 16~~ D7536 – 20

Standard Test Method for Chlorine in Aromatics by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D7536; 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 the determination of chlorine by ~~monochromatic,~~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 0.66 mg/kg to 10.07~~to 10 mg/kg. Higher chlorine concentrations can be determined by quantitatively diluting the sample with a suitable solvent. ~~In an interlaboratory study,~~ The limit of detection (LOD) is 0.2 mg/kg and the limit of ~~detection was determined to be 0.18 mg/kg.~~quantitation is 0.7 mg/kg. With careful analytical technique or the measurement of replicates, or both, this method can be used to successfully analyze concentrations below the LOD.

NOTE 1—The maximum is the highest concentration from the interlaboratory study (ILS) and the LOD and LOQ were calculated from Performance Testing Program (PTP) data. See Table 3.

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 E29.

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard information, see Section 9.*

1.6 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

[1] This test method is under the jurisdiction of ASTM Committee D16 on ~~Aromatic Hydrocarbons~~ Aromatic, Industrial, Specialty 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.

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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Documents:*[3]
OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Terminology

3.1 See Terminology D4790 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 Kα 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 calibration curve, the cautions and recommendation in Section 6 should be carefully observed.

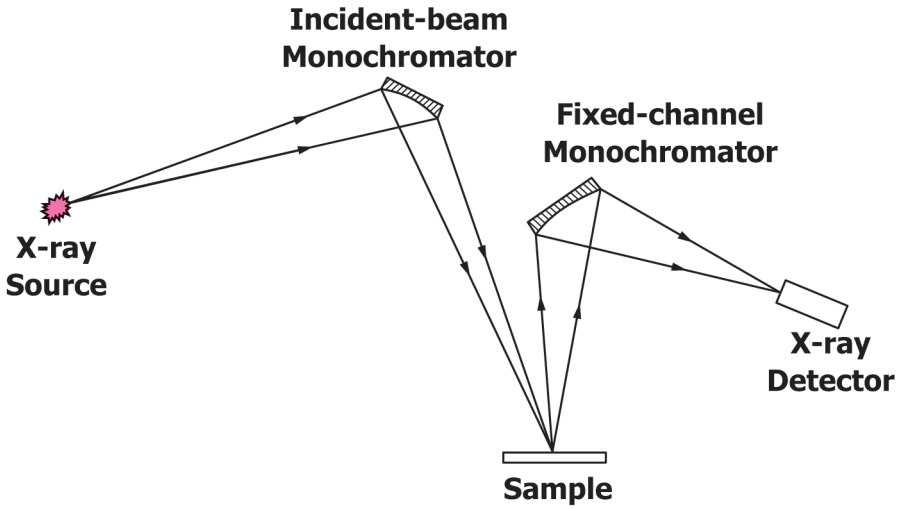

FIG. 1 Schematic of the MWDXRF Analyzer

[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.

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 Lα, Pd Lα, Ag Lα, Ti Kα, Sc Kα, and Cr Kα 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 Kα X-rays.

7.1.5 *Detector,* designed for efficient detection of chlorine Kα 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.

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[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,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, ~~D. C.~~ DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, ~~BD Ltd., Pole, Dourest, U. K.,~~ BDH Ltd., Poole, Dorset, U.K., and the *United States* ~~*Pharmacopoeia*~~*Pharmacopeia and National Formulary*, ~~U. S. Pharmaceutical~~ U.S. Pharmacopeial Convention, Inc. ~~(SUPT.),~~(USPC), Rockville, MD.

8.3 *2-Propanol,* minimum 99 % purity, for cleaning of analyzer parts in the sample chamber that may become contaminated with spilled samples and other contaminants.

8.4 *1,2,4-Trichlorobenzene,* a high-purity liquid (minimum 99 % purity) with a certified chlorine concentration. Use the certified chlorine concentration when calculating the exact concentrations of chlorine in calibration standards.

8.5 *Quality-Control Samples,* for use in establishing and monitoring the stability and precision of an analytical measurement system (see Section 17). Use homogeneous materials, similar to samples of interest and available in sufficient quantity to be analyzed regularly for a long period of time.

NOTE 2—Verification of system control through the use of QC samples and control charting is highly recommended.

NOTE 3—Suitable QC samples can be prepared by combining retains of typical samples.

8.6 *Xylene,* use a high purity *p*-xylene HPLC grade and account for its chlorine content when calculating the chlorine concentration of the calibration standards.

8.7 *Drift-Monitor Sample (optional),* to determine and correct instrument drift over time (see 12.4, 13.2, and 14.2). Various forms of stable chlorine-containing materials are suitable drift-correction samples, for example, liquid petroleum, solid, and pressed powder. The count rate displayed by the monitor sample, in combination with a convenient count time (T), shall be sufficient to give a relative standard deviation (RSD) of <1 % (see Appendix X1).

NOTE 4—Calibration standards may be used as drift-monitor samples.

NOTE 5—Because it is desirable to discard test specimens after each determination, a lower cost material is suggested for daily use. Any stable material can be used for daily monitoring of drift.

NOTE 6—The effect of drift correction on the precision and bias of this test method has not been studied.

9. Hazards

9.1 **Warning—**~~Warning~~Exposure~~—Exposure~~ to excessive quantities of X-ray radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of his/her body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with the regulations governing the use of ionizing radiation.

9.2 Consult current OSHA regulations, suppliers' Safety Data Sheets and local regulations for all materials used in this test method.

10. Sampling and Handling

10.1 Sample the material in accordance with Practice D3437.

10.2 For each sample, an unused piece of X-ray transparent film is required for the sample cell. Avoid touching the inside of the sample cell, any portion of the film exposed to the liquid or the X-ray beam, and also avoid touching the instrument window. Oil from fingerprints and wrinkles can generate errors in the analysis of chlorine. Therefore, make sure the film is taut and clean to ensure reliable results. It is recommended to use canned air to ensure the film and sample cup is dust free prior to assembling sample cell. Use calibration-check samples (see 8.2) to verify calibration integrity if the type and thickness of the window film is changed. After the sample cell is filled, provide a vent above the sample to prevent bowing of the film by accumulating vapors. When reusable sample cells are used, thoroughly clean and dry cells before each use. Disposable sample cells shall not be reused.

10.3 Because impurities and thickness variations can occur in commercially available transparent films and vary from lot to lot, use calibration-check samples (see 8.2) to verify calibration integrity after starting each new batch of film.

11. Preparation of Apparatus

11.1 *Analyzer Preparation*—Ensure that the MWDXRF analyzer has been installed and put into operation in accordance with

manufacturer's instructions. Allow sufficient time for instrument electronics to stabilize. Perform any instrument checkout procedures required. When possible, the instrument should be run continuously to maintain optimum stability.

11.1.1 Use the count time (T) recommended by the instrument manufacturer for the lowest chlorine concentration expected. The typical time for each measurement is five or ten minutes.

11.1.2 Alternatively, determine T expected for a desired count precision by following the procedure in Appendix X1.

11.2 *Minimizing Analyzer Contamination*—Analyzer contamination may lead to falsely high measurement results. To minimize analyzer contamination, perform the following steps at least once each day the analyzer is in use.

11.2.1 Clean the portion of the lid that is in contact with the top of the sample cell with 2-propanol. Additionally, clean the lid after measurement of a sample containing greater than 50 mg/kg chlorine and prior to the measurement of sample containing less than 1 mg/kg chlorine. Residue from higher concentration samples may contaminate subsequent low concentration measurements. Wipe up any visible sample residue after sample measurement.

11.2.2 Clean the primary window with 2-propanol soaked foam tipped or cotton swab. Shake excess alcohol from swab prior to using it for cleaning, as excess alcohol on the swab may leave a residue on the primary window when it dries. ~~I~~It is recommended to use canned air to blow the window dry. For analyzers with disposable primary windows, change the window instead of cleaning it.

11.2.3 Clean the sample basket with 2-propanol. Additionally, clean the sample basket any time the sample cell leaks in the measurement chamber.

11.2.4 If the analyzer is equipped with a secondary window, change the film. It is recommended to use canned air to ensure the film is dust free prior to reassembling the secondary window. Periodically inspect the secondary window and change if wrinkled, dirty, torn, or if there is a sample cell leak in the measurement chamber. Additionally, change the secondary window after measurement of a sample containing greater than 50 mg/kg chlorine prior to the measurement of samples containing less than 1 mg/kg chlorine. Residue vapors from higher concentration samples may be absorbed by the film and contaminate subsequent low concentration measurements.

12. Calibration

12.1 *Stock Solution*—Prepare a 1000 mg/kg chlorine in *p*-xylene stock solution by weighing approximately 0.15 g of 1,2,4-trichlorobenzene to the nearest 0.0001 g into a 100 mL volumetric flask. Dilute to the mark with chlorine free *p*-xylene. Calculate the actual concentration of the stock solution by using the equation:

$$mg/kg\ chlorine = (weight\ of\ trichlorobenzene\ in\ g * 0.5861 * 1\,000\,000)/86.1 \quad (1)$$

where:

0.5861 = % chlorine in trichlorobenzene/100, and
~~*86.1* = weight of 100 mL of *p*-xlyene (density = 0.861 g/mL).~~
86.1 = weight of 100 mL of *p*-xylene (density = 0.861 g/mL).

12.1.1 Alternate stock solutions may be prepared as long as the concentration is accurately calculated.

12.2 Prepare a minimum of 4 calibration standards by quantitatively diluting the stock solution with chlorine-free *p*-xylene. For example, 1 mL of the stock solution prepared in 12.1 diluted to 100 mL with *p*-xylene in a 100 mL volumetric flask will give a calibration standard of 10.0 mg/kg chlorine. Approximate recommended nominal chlorine concentration standards are listed as follows for the scope of this test method: 0.0 mg/kg (base material), 0.5 mg/kg, 1.0 mg/kg, 5.0 mg/kg, 10.0 mg/kg, and 50.0 mg/kg. Following instrument manufacturer's instructions in 13.3, measure the chlorine fluorescence intensity (total chlorine count rate) for each of the calibration standards. Convert total counts to count rate (R_S) in counts per second by dividing total counts by the count time (T) using units of seconds (see 11.1.1 and 11.1.2).

NOTE 7—Due to the linearity of the MWDXRF spectrometer calibration, it is recommended to calibrate beyond the scope of this test method in order to minimize negative effects at the lower end of the calibration of any errors in the preparation of calibration standards. For example, if one assumes an

absolute 1 mg/kg error in the preparation of each of the calibration standards, the relative error is minimized in the higher calibration standards (2 % error in the 50 mg/kg standard versus 20 % error in the 5 mg/kg standard). In effect, the higher calibration points serve to stabilize the slope of the calibration.

12.2.1 Alternately, commercially available calibration standards may be used provided their relative uncertainty does not exceed 1 %.

12.3 Construct a linear calibration model by either:

12.3.1 Using the software supplied by the instrument manufacturer, or

12.3.2 Do a linear regression of the calibration measurements. The linear equation:

$$R_S = Y + (E \times S) \quad (2)$$

describes the regression where:

R_S = measured total count rate (counts per second) of the chlorine fluorescence from 12.2,
Y = y-intercept of the calibration curve (counts per second),
E = slope of the calibration curve (counts kg s^{-1} mg^{-1}), and
S = chlorine concentration (mg/kg).

12.4 When using drift correction, measure the total counts of chlorine fluorescence from the drift-monitor sample during the calibration procedure. Determine R_S by dividing the total counts by T. The factor, R_S, determined on the drift-monitor sample at the time of calibration, is factor "A" in Eq 3 in 14.1.

12.5 Immediately after analyzing the calibration standards, determine the chlorine concentration of one or more calibration-check samples (see 8.2). The determined value shall be in the range defined by the certified concentration ± the repeatability of this test method. If this criterion is not met, the calibration process and calibration standards are suspect, corrective measures must be taken, and the calibration rerun. The degree of matrix mismatch between calibration check samples and standards should be considered when evaluating a calibration curve.

13. Procedure

13.1 *Specimen Preparation*—Prepare a specimen of a test sample or a calibration standards as follows:

13.1.1 Carefully transfer a sufficient portion of the liquid to fill an open-ended sample cell above a minimum depth of 3 mm, beyond which additional liquid does not affect the count rate. Filling the sample cell to three-fourths of the cell's depth is generally adequate.

13.1.2 Fit an unused piece of X-ray-transparent film over the sample-cell opening and attach securely. Use the same batch of film for the analysis of test samples and the calibration standards used for constructing the calibration curve. Avoid touching the inside of the sample cell, any portion of the film exposed to the liquid or the X-ray beam, and also avoid touching the instrument window. (It is highly recommended that clean, disposable rubber or plastic gloves be used when preparing test specimens.) Ensure the film is taut, wrinkle-free, and the sample is not leaking.

13.1.3 Provide a small vent to prevent bowing of the window film caused by the accumulating vapor. Many commercially available sample cells provide a means to vent the space above the liquid.

13.1.4 Perform the analysis of the specimen promptly after preparing the specimen. Do not let the specimen remain in the sample cell any longer than necessary before collecting the data.

13.2 When using drift correction, prior to analyzing samples on a given day, analyze the drift-monitor sample measured at the time of calibration. Divide the total counts measured on the drift-monitor sample by T to convert to R_S; this R_S corresponds to factor "B" in Eq 3 in 14.1.

13.3 Analyze each sample of interest as follows:

13.3.1 Prepare a test specimen of the sample of interest in accordance with 13.1.

13.3.2 Place the sample cell containing the test specimen in the X-ray beam, as directed in the instrument manufacturer's instructions. Allow the X-ray optical path to come to equilibrium.

13.3.3 Measure the total counts of chlorine fluorescence and divide the total counts by T to calculate R_S.

13.4 If R_S for a test specimen is greater than the highest count rate in the calibration curve, quantitatively dilute a fresh portion of the sample with the base material used to prepare the calibration standards. Dilute the sample so the resultant count rate is within the limits of the calibration curve. Repeat the procedures described in 13.3 on a test specimen of the diluted sample.

13.5 Calculate the concentration of chlorine in the test specimen as instructed in Section 14, taking into account any dilution factor from 13.4 (see 14.4).

14. Calculation

14.1 The instrument will automatically calculate the chlorine concentration if the instrument's software is used to calibrate the method.

14.2 When using a drift monitor sample, calculate a drift correction factor (F) for changes in daily instrument sensitivity in accordance with Eq 2. If a drift monitor is not used, F is set equal to 1.

$$F = A/B \tag{3}$$

where:

A = R_S for the drift monitor sample determined at the time of calibration (12.4) and
B = R_S for the drift monitor sample determined at the time of analysis (13.2).

14.3 Calculate the drift-corrected count rate (R_{cor}) for the test specimen as follows:

$$R_{cor} = F \times R_S \tag{4}$$

where:

F = drift correction factor, calculated by Eq 3 and
RS = total count rate for test specimen.

14.4 Calculate the chlorine content (S) of the test specimen by using the drift-corrected count rate (R_{cor}) in place of R_S in Eq 2 of 12.3.2.

14.5 If the test specimen was prepared from a quantitatively diluted sample, correct the measured concentration for sample dilution. The chlorine concentration (S_o) in the original, undiluted sample is calculated as follows:

$$S_o = [S_d \times (M_o + M_b)/M_o] - [S_b \times (M_b/M_o)] \tag{5}$$

where:

S_d = concentration of chlorine (mg/kg) in test specimen of the diluted sample (from 12.3),
M_o = mass (in g) of original sample,
M_b = mass (in g) of base material used to dilute sample, and
S_b = concentration of chlorine (mg/kg) in diluent.

15. Report

15.1 Report ~~chlorine concentration~~ the chlorine result as mg/kg of the ~~test sample calculated from Section~~ sample ~~14 using units of mg/kg, rounded~~ to the nearest ~~0.10~~0.1 mg/kg. Indicate that the results were obtained in accordance with Test Method D7536.

15.1.1 Results below 0.2 mg/kg should be reported as <0.2 mg/kg.