Designation: D7751 – 11$^{\varepsilon 1}$

Standard Test Method for Determination of Additive Elements in Lubricating Oils by EDXRF Analysis[1]

This standard is issued under the fixed designation D7751; 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.

ε[1] NOTE—Added research report footnote editorially in November 2011.

1. Scope

1.1 This test method covers the quantitative determination of additive elements in unused lubricating oils and additive packages, as shown in Table 1. The pooled limit of quantitation of this test method as obtained by statistical analysis of interlaboratory test results is 0.02% for magnesium, 0.003 % for phosphorus, 0.002 % for sulfur, 0.001 % for chlorine, 0.003 % for calcium, 0.001 % for zinc, and 0.002 % for molybdenum.

1.2 Additive packages require dilution with a contamination free diluent (base oil) prior to analysis. The dilution factor has to be calculated from the expected concentrations to bring the concentrations for all elements into the ranges listed in Table 1.

1.3 Some lubrication oils will contain higher concentrations than the maximum concentrations listed in Table 1. These samples require dilution with a contamination free diluent (base oil) prior to analysis. The dilution factor has to be calculated from the expected concentrations to bring the concentrations for all elements into the ranges listed in Table 1.

1.4 This test method is limited to the use of energy dispersive X-ray fluorescence (EDXRF) spectrometers employing an X-ray tube for excitation in conjunction with the ability to separate the signals of adjacent elements by using a high resolution semiconductor detector.

1.5 This test method uses inter-element correction factors calculated from a fundamental parameters (FP) approach or from another matrix correction method.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6.1 The preferred concentration units are mg/kg or mass %.

1.7 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

E1621 Guide for X-Ray Emission Spectrometric Analysis

2.2 *ISO Standards:*[3]

ISO 4259 Determination and application of precision data in relation to methods of test

3. Terminology

3.1 *Definitions:*

3.1.1 *energy dispersive X-ray spectrometry, n*—XRF spectrometry applying energy dispersive selection of radiation.

3.2 *Abbreviations:*

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Oct. 1, 2011. Published November 2011. DOI:10.1520/D7751-11E01.

[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] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

TABLE 1 Elements and Range of Applicability

Element	Concentration Range in mass %
Magnesium	0.02 to 0.4
Phosphorous	0.003 to 0.25
Sulfur	0.002 to 1.5
Chlorine	0.001 to 0.4
Calcium	0.003 to 1.0
Zinc	0.001 to 0.25
Molybdenum	0.002 to 0.05

3.2.1 *EDXRF*—Energy Dispersive X-ray Fluorescence Spectrometry.

3.2.2 *FP*—Fundamental Parameters.

4. Summary of Test Method

4.1 A specimen is placed in the X-ray beam, and the appropriate regions of its spectrum are measured to give the fluorescent intensities of magnesium, phosphorus, sulfur, chlorine, calcium, zinc, and molybdenum. Other regions of the spectrum are measured to compensate for matrix variation. To optimize the sensitivity for each element or group of elements, a combination of optimized excitation and detection conditions may be used (no more than two conditions should be used in order to keep the analysis time as short as possible, typically under ten minutes). There may be a correction of measured intensities for spectral overlap.

4.1.1 Concentrations of the elements of interest are determined by comparison of these intensities against a calibration curve using a fundamental parameters (FP) approach, possibly combined with corrections from backscatter. The FP approach uses the physical processes forming the basis of X-ray fluorescence emission in order to provide a theoretical model for the correction of matrix effects. The correction term is calculated from first principle expressions derived from basic physical principles and contain physical constants and parameters that include absorption coefficients, fluorescence yield, primary spectral distribution and spectrometry geometry. The calculation of concentrations in samples is based on making successively better estimates of composition by an iteration procedure.

NOTE 1—The algorithm used for the procedure is usually implemented in the instrument manufacturer's software.

4.2 The EDXRF spectrometer is initially calibrated using a set of standards to collect the necessary intensity data. Each calibration line and any correction coefficient are obtained by a regression of this data, using the program supplied with the spectrometer. (**Warning—**Exposure to excessive quantities of X-radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of their 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.)

5. Significance and Use

5.1 Lubricating oils are formulated with organo-metallic additives, which act, for example, as detergents, antioxidants, antifoaming, or antiwear agents, or a combination thereof. Some of these additives contain one or more of the following elements: magnesium, phosphorus, sulfur, chlorine, calcium, zinc, and molybdenum. This test method provides a means of determining the concentrations of these elements, which in turn provides an indication of the additive content of these oils.

5.2 Additive packages are the concentrates that are used to blend lubricating oils.

5.3 This test method is primarily intended to be used for the monitoring of additive elements in lubricating oils.

5.4 If this test method is applied to lubricating oils with matrices significantly different from the calibration materials specified in this test method, the cautions and recommendations in Section 6 should be observed when interpreting the results.

6. Interferences

6.1 The additive elements found in lubricating oils will affect the measured intensities from the elements of interest to a varying degree. In general the X-radiation emitted by the element of interest can be absorbed by itself (self-absorption) or by the other elements present in the sample matrix. Also the X-radiation emitted from one element can further excite (enhance) another element. These inter-element effects are significant at concentrations varying from 0.03 mass %, due to the higher atomic number elements (for example, molybdenum), to 1 mass %, for the lower atomic number elements (for example, sulfur). If an element is present at significant concentrations and an inter-element correction for that element is not employed, the results can be low due to absorption or high due to enhancement.

6.2 Absorption and enhancements effects will be corrected by corrections from the FP approach or by other matrix correction models.

6.3 There can be spectral overlap of one element onto another, and the instrument must include correction procedures for any such overlaps.

7. Apparatus

7.1 *Energy Dispersive X-ray Fluorescent Spectrometer*—Any energy dispersive X-ray fluorescence spectrometer can be used if its design incorporates at least the following features:

7.1.1 *Source of X-ray Excitation*—X-ray tube with palladium, silver, rhodium, or tungsten target. Other targets may be suitable as well. The voltage of the X-ray tube shall be programmable between 4 and at least 30 kV for preferential excitation of elements or groups of elements.

7.1.2 *X-ray Detector*—Semiconductor detector with high sensitivity and a spectral resolution value not to exceed 175 eV at 5.9 keV.

7.1.3 *Primary Beam Filters (Optional)*—To make the excitation more selective and to reduce the intensity of background radiation.

7.1.4 *Secondary or Polarization Targets, or Both (Optional)*—To make the excitation more selective and to improve peak-to-background ratio.

7.1.5 *Signal Conditioning and Data Handling Electronics*—That include the functions of X-ray intensity counting, spectra handling by background variation correction, overlap corrections, inter-elements effects corrections, and conversion of X-ray intensity into concentration.

7.1.6 *Helium Purgeable Optical Path (Optional)*—Helium purge improves the sensitivity of low energy X-rays emitted from low atomic number elements (Z< 22).

7.1.7 *Sample Cells*—Providing a depth of at least 6 mm and equipped with replaceable X-ray transparent film.

7.1.8 *Sample Film*—Suitable films include polypropylene, polyester, and polycarbonate with thickness from 3.5 to 8 µm. A thick film may limit the performance for low atomic numbers (for example, Magnesium).

7.2 *Instrument Setting-Up Samples (Elemental Reference Samples) (Optional)*—To quantify spectral overlaps. These are not required when the instrument's software does include software to deconvolute spectra.

7.3 *Drift Correction Monitors (Optional)*—To correct for instrumental drift. At least two samples are necessary to correct both sensitivity and possible changes in the background. For each element and scatter region, there shall be one providing a count rate similar to samples from the upper end of the calibration and another providing a count rate as if from a blank. This last can be a blank oil. For the high concentration of each element, a glass disk, XRF fusion bead, or pressed pellet have all been found to be satisfactory. Elemental reference samples (7.2) may also be used.

7.3.1 Drift correction is usually implemented automatically in software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from unity.

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

7.5 For additional information, also refer to Practice D7343.

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

8. Reagents and Materials

8.1 *Purity of Reagents*[4]—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. 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 *Diluent Solvent*—A suitable solvent containing less than 10 mg/kg of sulfur and containing less than 1 mg/kg of metals as well as of all other elements of interest (for example, base oil).

8.3 *Helium Gas*—Minimum purity 99.9 %.

8.4 *Calibration Standard Materials:*

8.4.1 Commercially available calibration solutions.

8.4.2 Certified concentration solutions, of liquid organometallic salts, the following standard materials can be used:

8.4.2.1 *Calcium 2-Ethylhexanoate,* approximately 12.3 mass % calcium.

8.4.2.2 *Zinc Cyclohexanebutyrate,* approximately 16.2 mass % zinc.

8.4.2.3 *Bis(2-Ethylhexyl)Hydrogen Phosphate,* 97 % purity (approximately 9.62 mass % phosphorus).

8.4.2.4 *Di-n-butyl Sulfide,* 97 % purity (approximately 21.9 mass % sulfur).

8.4.2.5 *Magnesium-2-ethylhexoate,* (2.99 % magnesium).

8.4.2.6 *1-Chlorooctane,* 98 % purity, (23.9 mass % chlorine).

8.4.2.7 Commercially available single element standard for molybdenum based on molybdenumsulfonate.

8.4.2.8 *Stabilizers,* 2-ethylhexanoic acid, 2-ethylamine, also proprietary stabilizer/chelating solutions are available commercially. Stabilizers shall be free of the additive element.

NOTE 3—In addition to the calibration standard materials identified in 8.4, single or multielement calibration standards can also be prepared from materials similar to the samples being analyzed, provided the calibration standards to be used have previously been characterized by independent primary (for example, gravimetric or volumetric) analytical techniques to establish the elemental concentration mass % levels.

9. Hazards

9.1 Occupational health and safety standards for X-rays and ionizing radiation shall be observed. It is also recommended that proper practices be followed as presented by most manufactures documentation or described in Guide E1621.

10. Sampling and Test Specs and Units

10.1 Samples shall be taken in accordance with the instructions in Practices D4057 or D4177. For sample handling, also refer to Practice D7343.

10.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused. For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, the portion of the window film in the cell, or the instrument window that is exposed to X-rays. Oil from fingerprints can affect the reading when determining low levels of analytes. Wrinkles in the film will affect the intensity of the X-rays transmitted, therefore, it is essential that the film be taut and clean to ensure reliable results. When handling the window film, avoid touching the central part (the part that actually forms the optical window) as this can lead to contamination from sweat, grease or other petrochemical products. Discard film that has been exposed to the atmosphere (for example, hanging outside of the film roll dispensing box). The analyzer may need recalibration if the type or thickness of the window

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.