Designation: D 6481 – 99

An American National Standard

Standard Test Method for
Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive X-ray Fluorescence Spectroscopy[1]

This standard is issued under the fixed designation D 6481; 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 quantitative determination of additive elements in unused lubricating oils, as shown in Table 1.

1.2 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.

1.3 This test method uses interelement correction factors calculated from empirical calibration data.

1.4 This test method is not suitable for the determination of magnesium and copper at the concentrations present in lubricating oils.

1.5 This test method excludes lubricating oils that contain chlorine or barium as an additive element.

1.6 This test method can be used by persons who are not skilled in X-ray spectrometry. It is intended to be used as a routine test method for production control analysis.

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 to use.* (See Note 1.)

2. Summary of Test Method

2.1 A specimen is placed in the X-ray beam, and the appropriate regions of its spectrum are measured to give the fluorescent intensities of phosphorus, sulfur, calcium, and zinc. Other regions of the spectrum are measured to compensate for varying background. If the detector does not completely resolve all the elements in a single measurement, then to improve selectivity, there is a combination of sequential and simultaneous measurements employing primary and secondary beam filters. There can be correction of measured intensities for spectral overlap. Concentrations of the elements of interest are determined by comparison of these intensities against a calibration curve using empirical interelement correction factors and ratio to backscatter.

2.2 The EDXRF spectrometer is initially calibrated using a set of prepared 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.

TABLE 1 Elements and Range of Concentrations Determined

Element	Concentration Range
Phosphorus	0.02 to 0.3 mass %
Sulfur	0.05 to 1.0 mass %
Calcium	0.02 to 1.0 mass %
Zinc	0.01 to 0.3 mass %

3. Significance and Use

3.1 Some oils are formulated with organo-metallic additives, which act, for example, as detergents, antioxidants, and antiwear agents. Some of these additives contain one or more of these elements: calcium, phosphorus, sulfur, and zinc. 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.

3.2 This test method is primarily intended to be used at a manufacturing location for monitoring of additive elements in lubricating oils. It can also be used in central and research laboratories.

4. Interferences

4.1 The additive elements found in lubricating oils will affect the measured intensities from the elements of interest to a varying degree. In general, for lubricating oils, 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 interelement effects are significant at concentrations varying from 0.03 mass %, due to the heavier elements, to 1 mass %, for the lighter elements. Enhancement effects can be minimised by selective excitation. The measured concentration for a given element can be mathematically corrected for self-absorption

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[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.

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and for interelement effects by other elements present in the sample matrix. 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.

4.2 If a sample containing barium as an additive above 0.03 mass % is measured against a calibration derived from standards without barium, then results will be low.

4.3 If a sample containing chlorine as an impurity above 0.03 mass % is measured against a calibration derived from standards without chlorine, then the results can be affected.

4.4 There can be spectral overlap of one element onto another, especially for phosphorus on sulfur, and the instrument must include correction procedures for any such overlaps.

5. Apparatus

5.1 *Energy Dispersive X-ray Fluorescent Analyzer*—Any energy dispersive X-ray fluorescent analyzer can be used if its design incorporates at least the following features.

5.1.1 *Source of X-ray Excitation*, X-ray tube with palladium, silver, or rhodium target programmable between 4 and at least 25 keV for preferential excitation to simplify the sample spectra. (**Warning**—Operation of an analyzer using an X-ray tube source is to be conducted in accordance with the manufacturer's safety instructions and federal, state, and local regulations)

5.1.2 *X-ray Detector*, gas filled proportional counter with high sensitivity and a resolution value not to exceed 1300 eV at 5.9 keV.

NOTE 1—The limited data from instruments with solid state detectors in the inter-laboratory precision study did not support their inclusion in the method.

5.1.3 *Primary Beam Filters*, to make the excitation more selective.

5.1.4 *Secondary Beam Filters*—When a proportional counter is used, these are necessary as a means of discriminating between an analyte's X-rays and other analytes and the spectrum from the X-ray tube.

5.1.5 *Multi-channel Analyzer*, for discrimination between an analyte's X rays and background X rays.

5.1.6 *Optional Helium Purgeable Optical Path*.

5.2 *Sample Cells*, providing a depth of at least 6 mm and equipped with replaceable X-ray transparent film. Suitable films include polypropylene and polycarbonate with thickness from 3.5 to 8 μm.

5.3 *Instrument Setting Up Samples (Elemental Reference Samples)*, to quantify spectral overlaps. These are required when the instrument's software does not include reference spectra to deconvolute spectra.

5.4 *Drift Correction Monitors*, to correct for instrumental drift. At least two samples are necessary to correct both sensitivity and baseline drifts. 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. They can be the same samples as in 5.3

6. Reagents and Materials

6.1 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.[2] Other grades can 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.

6.2 *Helium*, at least 99.5 % purity, for the optical path of the spectrometer.

6.3 *Diluent Solvent*, a suitable solvent free of metals, phosphorus, and chlorine and containing less than 10 ppm of sulfur (for example, deodorized kerosene, white oil, or mineral oil).

6.4 *Calibration Standard Materials*:

6.4.1 Certified concentration solutions[3] of liquid organo-metallic salts, each containing calcium or zinc, or both. The solutions shall be sulfur free or the certificate shall state the concentration of sulfur. Alternatively, the following standard materials can be used.

6.4.1.1 *Calcium 2-Ethylhexanoate*, approximately 12.3 mass % calcium, with a certified value.

6.4.1.2 *Zinc Cyclohexanebutyrate*, approximately 16.2 mass % zinc, with a certified value.

6.4.2 *Bis(2-Ethylhexyl)Hydrogen Phosphate*, 97 % purity (9.62 mass % phorphorus).

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

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

NOTE 2—In addition to the calibration standard materials identified in 6.4.1-6.4.3, 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.

7. Preparation of Calibration Standards

7.1 To ensure complete solution of all components, prepare calibration standards by precisely weighing the organo-metallic solutions and phosphorus and sulfur solutions with the diluent solvent along with the appropriate stabilizer. Table 2 lists suggested concentrations when determining empirical influence coefficients. Complete sets of standards based on Table 2 are commercially available.

8. Calibration

8.1 *Spectrometer Settings*—Follow the manufacturer's recommendations and set up a series of measurement conditions, (X-ray tube voltage, X-ray tube current, primary beam filter,

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[2] *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 *Analar 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.

[3] These certified concentrated solutions are commercially available.