



Designation: D6481 – 24

Standard Test Method for Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive X-ray Fluorescence Spectroscopy¹

This standard is issued under the fixed designation D6481; 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, health, and environmental practices and determine the applicability of regulatory limitations to use.*

1.8 *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.*

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

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2. Referenced Documents

- 2.1 *ASTM Standards*:²
[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

3. Terminology

- 3.1 *Definitions*:

3.1.1 For definitions of terms used in this test method, refer to Terminology [D4175](#).

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 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.

4.2 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.

5. Significance and Use

5.1 Some oils are formulated with organo-metallic additives, which act, for example, as detergents, antioxidants,

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

TABLE 1 Elements and Range of Concentrations Determined

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

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.

5.2 Several additive elements and their compounds are added to the lubricating oils to give beneficial performance (Table 2).

5.3 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.

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, 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 % by mass, due to the heavier elements, to 1 % by mass, for the lighter elements. Enhancement effects can be minimized by selective excitation. The measured concentration for a given element can be mathematically corrected for self-absorption 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.

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

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

6.4 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.

7. Apparatus

7.1 *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.

7.1.1 *Source of X-ray Excitation*, X-ray tube with palladium, silver, or rhodium target programmable between 4 keV 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.)

7.1.2 *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 interlaboratory precision study did not support their inclusion in this test method.

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

7.1.4 *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.

7.1.5 *Multi-Channel Analyzer*, for discrimination between an analyte’s X rays and background X rays.

7.1.6 *Optional Helium Purgeable Optical Path*.

7.2 *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 μm to 8 μm .

7.3 *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.

7.4 *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

TABLE 2 Lubricants and Additive Materials

Element	Compounds	Purpose/Application
Calcium	Sulfonates, phenates	Detergent inhibitors, dispersants
Phosphorus	Dithiophosphates, phosphates phosphites	Anti-rusting agents, extreme pressure additives, anti-wear
Sulfur	Base oils, sulfonates, thiophosphates, polysulfides and other sulfurized components	Detergents, extreme pressure additives, anti-wear
Zinc	Dialkylidithiophosphates, dithiocarbamates, phenolates carboxylates	Anti-oxidant, corrosion inhibitors, antiwear additives, detergents, crankcase oils, hypoid gear lubricants, aircraft piston engine oils, turbine oils, automatic transmission fluids, railroad diesel engine oils, brake lubricants