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.

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 %

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.

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 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

[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 Nov. 10, 1999. Published January 2000.

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 organometallic 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 organometallic 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, secondary beam filter, measurement time, and multichannel analyzer region of interest) to measure the •K spectrum of phosphorus, sulfur, calcium, and zinc. Include at least one region of backscatter.

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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.

TABLE 2 Recommended Concentrations for Standards (all values mass %)

Standard	Calcium	Phosphorus	Sulfur	Zinc
1	0	0	0	0
2	0.005	0.005	0.050	0.05
3	0.600	0	0	0
4	0	0.300	0	0
5	1.00	0	1.00	0
6	0	0	0	0.300
7	0.005	0.250	0.800	0.300
8	0.500	0.150	0.500	0.150
9	0.010	0.200	0.100	0.250
10	0.050	0.010	0.400	0.075
11	0.100	0.150	0.200	0.200
12	0.200	0.200	0.800	0.100
13	0.400	0.005	0.800	0.300
14	0.600	0.100	0.500	0.050
15	0.800	0.010	0.050	0.100
16	1.00	0.300	1.00	0.150
17	0.400	0.050	0.600	0.250

8.2 Fill respective sample cells nearly full with the calibration standard solutions. Follow the manufacturer's recommendation to ensure that the cell is full enough such that X-ray count rate does not depend on the amount of sample in the cell. Make sure that no wrinkles or bulges are present in the film. The film must be flat, and the cell shall be vented.

8.3 Place the sample cell in the X-ray beam to measure and record the intensity for each element and scatter region in each calibration standard in accordance with the conditions set by following 8.1. Measure each standard two times, using a freshly prepared cell for each measurement.

8.4 Measure any instrument setting up samples necessary to quantify spectral overlaps. Use at least the measurement time of the calibration standards

8.5 Measure and record the intensity for each element and scatter region of the drift correction monitors. Use at least the measurement time of the calibration standards.

NOTE 3—An instrument setting up sample used in 8.4 can also be used as a drift correction monitor in 8.5 if its elemental composition is suitable.

8.6 Use the instrument's regression software to generate the optimum calibration curve for each element by applying the appropriate corrections. Suggested corrections are given in Table 3. The variable sulfur content results in a change in background for phosphorus because of filter fluorescence. (If a filter is not used, there will be a spectral overlap of sulfur on phosphorus and an overlap correction will be necessary). Sulfur also affects the sensitivity for calcium because of its high absorption for that element. Because phosphorus X rays have an energy below the absorption edge of the sulfur filter, it overlaps sulfur. (If a filter is not used, there will be also be a spectral overlap of phosphorus on sulfur). Zinc is the heaviest element in lubricating oil, and therefore, all matrix effects can in practice be corrected by taking a ratio to the high energy backscatter.

TABLE 3 Suggested Corrections for Optimum Calibrations

Element	Instrument Corrections	Inter-element effects
Phosphorus	Filter fluorescence by sulfur	None
Sulfur	Overlap by phosphorus	None
Calcium	None	Sulfur mass absorption
Zinc	None	Ratio to high energy backscatter

NOTE 4—No instruments in the interlaboratory precision study that established the precision statements used theoretical correction coefficients for mass absorption effects.

9. Procedure

9.1 Fill a sample cell nearly full with a portion of the sample to be analyzed. Follow the manufacturer's recommendation to ensure that the cell is full enough such that X-ray count rate does not depend on the amount of sample in the cell. Make sure that no wrinkles or bulges are present in the film. The film must be flat. The cell shall be vented, by cutting a hole in the top, if necessary.

9.2 Place the sample cell in the X-ray beam to measure and record the intensity for each element and scatter region in each calibration standard in accordance with the conditions set by following 8.1.

10. Calculation

10.1 Set the instrument's software to calculate the results in mass % to three decimal places.

11. Report

11.1 Report the following information:

11.1.1 Total content for each element, phosphorus, sulfur, calcium, and zinc in mass %.

11.1.2 State that the results were obtained by Test Method D xxxx.

12. Quality Control (QC)

12.1 Typically, one or more stable QC samples that are similar in composition to test samples are analyzed regularly by the testing laboratory. Because data quality requirements can vary among testing laboratories, individual laboratories can determine the frequency of QC sample analysis and the acceptable control limits.

12.2 When QC results are not within control limits, carry out corrective action, such as drift correction or recalibration, or both.

12.3 The QC sample precision can be compared with precision of this test method to determine data quality.

13. Precision and Bias

13.1 *Precision*—The precision of this test method as obtained by statistical analysis of interlaboratory test results is as follows.

13.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in Table 4 in only one case in twenty.

TABLE 4 Repeatability of Each Element

Element	Repeatability Mass %
Phosphorus	0.0060
Sulfur	$0.01648(X^A + 0.0141)^{0.8}$
Calcium	$0.008795(X + 0.0120)^{0.5}$
Zinc	$0.003274\ X^{0.25}$

[A] X is the concentration of the element in mass %.

13.1.2 *Reproducibility*—the difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values in Table 5 in only one case in twenty.

NOTE 5—The values of the precision estimates for selected values of *X*, in Tables 4 and 5, are set out in Table 6.

13.2 *Bias*—No information can be presented on the bias of the procedure in Test Method D xxxx for measuring phosphorus, sulfur, calcium, and zinc because no material having an accepted reference value is available.

14. Keywords

14.1 additive elements; additives; calcium; energy dispersive; lubricating oils; phosphorus; spectrometry; sulfur; X ray; zinc

TABLE 5 Reproducibility of Each Element

Element	Reproducibility mass %
Phosphorus	0.0199
Sulfur	$0.1024(X^A + 0.0141)^{0.8}$
Calcium	$0.1492(X + 0.0120)^{0.5}$
Zinc	$0.02165\ X^{0.25}$

[A] *X* is the concentration of the element in mass %.

TABLE 6 Repeatability and Reproducibility

Mass % (*X*)	Repeatability	Reproducibility
Phosphorus		
0.02	0.006	0.020
0.05	0.006	0.020
0.15	0.006	0.020
0.3	0.006	0.020
Sulfur		
0.05	0.002	0.011
0.10	0.003	0.018
0.50	0.010	0.060
1.0	0.017	0.104
Calcium		
0.02	0.002	0.027
0.05	0.002	0.037
0.10	0.003	0.050
0.50	0.006	0.107
1.0	0.009	0.150
Zinc		
0.01	0.001	0.007
0.05	0.002	0.10
0.10	0.002	0.012
0.15	0.002	0.014
0.3	0.002	0.016

APPENDIX

(Nonmandatory Information)

X1. AIDS TO ANALYST

X1.1 Avoid using sample cell films other than the ones recommended. Polyester films may contain impurities of silicon, phosphorus, and calcium.

X1.2 If the instrument uses a secondary safety window, ensure that it is clean before each sample. If in doubt, then change it.

X1.3 Avoid contamination of the sample cell window. Do not touch it.

X1.4 Ensure sample cell windows are flat and free of wrinkles.

X1.5 When a new container or batch of sample film is used, check the method with the QC check sample.

X1.6 Establish a list of corrective actions that can be implemented when results from a QC test are outside control limits. Your instrument supplier may be able to advise on this.

X1.7 Analyze the diluent solvent as an additional QC sample from time to time to confirm that there is no contamination in the instrument.