



## Standard Test Methods for Elemental Analysis of Lubricant and Additive Components— Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy<sup>1</sup>

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*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 These test methods cover the determination of barium, calcium, phosphorus, sulfur, and zinc in unused lubricating oils at element concentration ranges from 0.03 to 1.0 mass % (0.01 to 2.0 mass % for sulfur). The range can be extended to higher concentrations by dilution of sample specimens. Additives can also be determined after dilution. Two different methods are presented in these test methods.

1.2 *Test Method A (Internal Standard Procedure)*—Internal standards are used to compensate for interelement effects of X-ray excitation and fluorescence (see Sections 1-11, and 16).

1.3 *Test Method B (Mathematical Correction Procedure)*—The measured X-ray fluorescence intensity for a given element is mathematically corrected for potential interference from other elements present in the sample (see Sections 1-6, and 12-16).

1.4 The preferred concentration units are mass percent barium, calcium, phosphorus, sulfur, or zinc.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Summary of the Test Methods

2.1 A sample specimen is placed in the X-ray beam and the intensity of the appropriate fluorescence lines of barium, calcium, phosphorus, sulfur, and zinc are measured. Instrument response factors related to the concentration of standards enable the determination of the concentration of elements in the tested sample specimens. Enhancement or depression of the X-ray fluorescence of a given element by an interfering element in the sample may occur. Two test methods (A and B) are described for compensating any interference effect.

2.2 *Test Method A (Internal Standard Procedure)*—Internal standards are used with the standards and sample specimens to

compensate for the potential interelement effects.

2.2.1 *Barium, Calcium, Phosphorus, and Zinc*—A sample specimen that has been blended with a single internal standard solution (containing tin or titanium for barium and calcium, zirconium for phosphorus, and nickel for zinc) is poured into an X-ray cell. Total net counts (peak intensity—background) for each element and its respective internal standard are collected at their appropriate wavelengths. The ratios between elemental and internal standard counts are calculated and converted into barium, calcium, phosphorus, or zinc concentrations, or a combination thereof, from calibration curves.

2.2.2 *Sulfur*—A sample specimen is mixed with a lead internal standard solution and analyzed as described in 2.2.1.

2.3 *Test Method B (Mathematical Correction Procedure)*—The measured intensity for a given element is mathematically corrected for the interference from other elements in the sample specimen. This requires that intensities from all elements in the specimen be obtained.

2.3.1 The sample specimen is placed in the X-ray beam and the intensities of the fluorescence lines of barium, calcium, phosphorus, sulfur, and zinc are measured. A similar measurement is made away from the fluorescence lines in order to obtain a background correction. Concentrations of the elements of interest are determined by comparison of net signals against appropriate interelement correction factors developed from responses of calibration standards.

2.3.2 The X-ray fluorescence spectrometer is initially calibrated with a suite of standards in order to determine by regression analysis, interelement correction factors and instrument response factors.

2.3.3 Subsequent calibration is achieved using a smaller number of standards since only the instrument response factors need to be redetermined. One of these standards (or an optional synthetic pellet) can be used to monitor instrumental drift when performing a high volume of analyses.

2.4 Additives and additive packages can be determined after dilution with base oil to place the elemental concentrations in the range described in 1.1.

### 3. Significance and Use

3.1 Some oils are formulated with organo-metallic additives which act as detergents, antioxidants, antiwear agents, and so

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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