Designation: D4927 – 10

Standard Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy[1]

This standard is issued under the fixed designation D4927; 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.

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 shown in Table 1. 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 8 through 13).

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 14 through 19).

1.4 The preferred concentration units are mass % 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. Referenced Documents

2.1 *ASTM Standards:*[2]

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

TABLE 1 Range of Applicability

Element	Range, Mass %
Barium	0.04-8.5
Calcium	0.01-1.0
Phosphorus	0.01-0.5
Sulfur	0.1-4.0
Zinc	0.01-0.6

3. Summary of the Test Methods

3.1 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.

3.2 *Test Method A (Internal Standard Procedure)*—Internal standards are used with the standards and sample specimens to compensate for the potential interelement effects.

3.2.1 *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.

3.2.2 *Sulfur*—A sample specimen is mixed with a lead internal standard solution and analyzed as described in 3.2.1.

3.3 *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.

[1] These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[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.**

3.3.1 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.

3.3.2 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.

3.3.3 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.

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

4. Significance and Use

4.1 Some oils are formulated with organo-metallic additives which act as detergents, antioxidants, antiwear agents, and so forth. Some of these additives contain one or more of these elements: barium, calcium, phosphorus, sulfur, and zinc. These test methods provide a means of determining the concentration of these elements which in turn provides an indication of the additive content of these oils.

5. Interferences

5.1 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 is absorbed by the other elements in the sample matrix. Also, the X-radiation emitted from one element can further excite another element. These effects are significant at concentrations varying from 0.03 mass % due to the heavier elements to 1 mass % for the lighter elements. The measured intensity for a given element can be mathematically corrected for the absorption of the emitted radiation by the other elements present in the sample specimen. Suitable internal standards can also compensate for X-ray inter-element effects. If an element is present at significant concentrations and an interelement correction for that element is not employed, the results can be low due to absorption or high due to enhancement.

6. Apparatus

6.1 *X-Ray Spectrometer*, equipped for soft X-ray detection of radiation in the range from 1 to 10 Å. For optimum sensitivity, the spectrometer is equipped with the following:

6.1.1 *X-Ray Generating Tube*, with chromium, rhodium, or scandium target. Other targets can also be employed.

6.1.2 *Helium*, purgeable optical path.

6.1.3 *Interchangeable Crystals*, germanium, lithium fluoride (LiF_{200}), graphite, or pentaerythritol (PET), or a combination thereof. Other crystals can also be used.

6.1.4 *Pulse-Height Analyzer*, or other means of energy discrimination.

6.1.5 *Detector*, flow proportional, or scintillation, or flow proportional and scintillation counter.

6.2 *Shaker, Mechanical Stirrer, or Ultrasonic Bath*, capable of handling from 30-mL to 1-L bottles.

6.3 *X-Ray Disposable Plastic Cells*, with suitable film window. Suitable films include Mylar,[3] polypropylene, or polyimid with film thicknesses between 0.25 to 0.35 mil (6.3 to 8.8 µm).

NOTE 1—Some films contain contamination of the elements of interest (Mylar in particular). The magnitude of the contamination is assessed and the same film batch used throughout the entire analysis.

7. Purity of Reagents

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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.

TEST METHOD A (INTERNAL STANDARD PROCEDURE)

8. Reagents and Materials

8.1 *Helium*, for optical path of spectrometer.

8.2 *P-10 Ionization Gas*, 90 volume % argon and 10 volume % methane for the flow proportional counter.

8.3 *Diluent Solvent*, a suitable solvent free of metals, sulfur, and phosphorus (for example, kerosine, white oil, or xylenes).

8.4 *Internal Standard Materials*:

8.4.1 *Nickel Octoate*, preferably containing 5.0 ± 0.1 mass % nickel. If the nickel concentration is higher or lower (minimum concentration that can be used is 2.5 ± 0.1 mass % nickel), the laboratory needs to adjust the amount of sample taken in 9.1 to yield an equivalent nickel concentration level in the internal standard. Other nickel-containing organic matrices (free of other metals, sulfur, and phosphorus) may be substituted provided the nickel is stable in solution, the concentration is known (≥2.5 ± 0.1 mass % nickel), and the laboratory can adjust the amount of sample taken in 9.1 to yield an equivalent nickel concentration level in the internal standard if the nickel concentration does not initially contain 5.0 ± 0.1 mass % nickel.

NOTE 2—Many X-ray tubes emit copper X rays which increase in intensity with age. This does not present a problem when using copper as an internal standard for zinc providing that frequent calibrations are

[3] A registered trademark of E. I. du Pont de Nemours and Co.

[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 *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.

performed. No problem exists when using nickel as internal for zinc and nickel is the preferred internal standard material.

8.4.2 *Titanium 2-Ethylhexoide or Tin Octoate*, preferably containing 8.0 ± 0.1 mass % titanium or tin. If the titanium or tin concentration is higher or lower (minimum concentration that can be used is 4.0 ± 0.1 mass % titanium or tin), the laboratory needs to adjust the amount of sample taken in 9.1 to yield an equivalent titanium or tin concentration level in the internal standard. Other titanium or tin containing organic matrices (free of other metals, sulfur, and phosphorus) may be substituted, provided the titanium or tin is stable in solution, the concentration is known (≥4.0 ± 0.1 mass % titanium or tin), and the laboratory can adjust the amount of sample taken in 9.1 to yield an equivalent titanium or tin concentration level in the internal standard if the titanium or tin concentration does not initially contain 8.0 ± 0.1 mass % titanium or tin.

8.4.3 *Zirconium Octoate*, preferably containing 12.0 ± 0.1 mass % zirconium. If the laboratory uses zirconium octoate with a lower mass % zirconium concentration level, the laboratory needs to evaporate away the petroleum solvent to yield a solution that contains 12.0 ± 0.1 mass % zirconium. Other zirconium containing organic matrices (free of other metals, sulfur, and phosphorus) may be substituted, provided the zirconium is stable in solution and the concentration is known and does not exceed 12.0 ± 0.1 mass % zirconium. If the zirconium concentration is <12.0 ± 0.1 mass %, the laboratory needs to evaporate away the petroleum solvent to yield a solution that contains 12.0 ± 0.1 mass % zirconium.

8.4.4 *Lead Naphthenate*, containing 24.0 ± 0.1 mass % lead.

8.5 *Calibration Standard Materials*:

NOTE 3—In addition to calibration standards identified in 8.5.1-8.5.5, single-element or multielement calibration standards may 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.

8.5.1 *Barium 2-Ethylhexoide or Sulfonate*, with concentrations ≥4 mass % barium and certified to better than ±0.1 % absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 10.1.1 and 10.1.2.

8.5.2 *Calcium Octoate or Sulfonate*, with concentrations ≥ 4 mass % calcium and certified to better than ±0.1 % absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 10.1.1 and 10.1.2.

8.5.3 *Bis(2-Ethylhexyl)Hydrogen Phosphate*, 97 % purity (9.62 mass % phosphorus). Other phosphorus containing organic matrices (free of other metals) may be substituted provided the phosphorus is stable in solution and the concentration is ≥4 mass % phosphorus and certified to better than ±0.1 % absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 10.1.1 and 10.1.2.

8.5.4 *Zinc Sulfonate or Octoate*, with concentration ≥4 mass % zinc and certified to better than ±0.1 % absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 10.1.1 and 10.1.2.

8.5.5 *Di-n-Butyl Sulfide*, 97 % purity, (21.9 mass % sulfur). Other sulfur containing organic matrices (free of metals) may be substituted, provided the sulfur is stable in solution and the concentration is ≥2 mass % sulfur and certified to better than ±0.1% absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 10.1.2.

8.6 *Quality Control (QC) Samples*, preferably are portions of one or more lubricating oils or additives that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process and performance of the instrument as described in Section 12.

9. Preparation of Internal Standards

9.1 *Barium, Calcium, Phosphorus, and Zinc*—Dispense 240 ± 0.5 g of nickel octoate (5.0 ± 0.1 mass % nickel), 30 ± 0.1 g of titanium 2-ethylhexoide (8.0 ± 0.1 mass % titanium) or 30 ± 0.1 g of tin octoate (8.0 ± 0.1 mass % tin), and 450 ± 1 g of diluent solvent into a 1-L bottle. Shake or stir the bottle for a minimum of 10 min. If the laboratory uses internal materials that have different elemental concentrations than those explicitly stated in 8.4.1 and 8.4.2, it will be necessary for the laboratory to adjust the amount of sample taken in order to obtain an equivalent elemental concentration in the internal standard blend that is prepared according to the following equations:

$$A = 240 \times (5/x) \quad (1)$$

$$B = 30 \times (8/y) \quad (2)$$

$$C = 720 - [A + B] \quad (3)$$

where:

A = nickel containing material in blend, g,
B = titanium or tin containing material in blend, g,
C = diluent to add to blend, g,
x = nickel in material chosen as an internal standard, mass %, and
y = titanium or tin in material chosen as an internal standard, mass %.

9.2 *Sulfur*—Lead naphthenate, 24 mass % lead, serves as a suitable internal standard. (**Warning**—Hazardous. Lead naphthenate is toxic and precautions should be taken to avoid inhalation of vapors, ingestion, or skin contact.) No further treatment of this compound is necessary.

10. Preparation of Calibration Standards

10.1 *Barium, Calcium, Phosphorus, and Zinc*:

10.1.1 For concentrations less than 0.1 mass %, prepare standards containing 0.00, 0.01, 0.025, 0.050, 0.075, and 0.10 mass % of each respective element in the diluent solvent.

10.1.2 For concentrations greater than 0.1 mass %, prepare standards containing 0.00, 0.10, 0.25, 0.50, 0.75, and 1.00 mass % of each respective element in the diluent solvent.

10.1.3 Dispense 1.000 ± 0.001 g of the zirconium internal standard solution described in 8.4.3 into a 30-mL bottle. Prepare an individual bottle for each of the calibration standards.

10.1.4 Dispense 1.000 ± 0.001 g of the internal standard solution described in 9.1 into a 30-mL bottle. Repeat for all of the calibration-standard bottles.