



Designation: D4927 – 14

# 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>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the U.S. 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:<sup>2</sup>

[D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)

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

Current edition approved Dec. 1, 2014. Published January 2015. Originally approved in 1989. Last previous edition approved in 2010 as D4927 – 10. DOI: 10.1520/D4927-14.

<sup>2</sup> 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.

## 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.

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.

\*A Summary of Changes section appears at the end of this standard

**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

3.3.2 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.

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

#### 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<sub>200</sub>), 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,<sup>3</sup> polypropylene, or polyimide 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

<sup>3</sup> A registered trademark of E. I. du Pont de Nemours and Co.

**TABLE 2 Lubricants and Additive Materials**

Element	Compounds	Purpose/Application
Barium	Sulfonates, Phenates	Detergent inhibitors, corrosion inhibitors, detergents, rust inhibitors, automatic transmission fluids
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	Dialkyldithiophosphates, Dithiocarbamates, Phenolates Carboxylates	Anti-oxidant, corrosion inhibitors, anti-wear additives, detergents, crankcase oils, hypoid gear lubricants, aircraft piston engine oils, turbine oils, automatic transmission fluids, railroad diesel engine oils, brake lubricants

Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> 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  $5.0 \pm 0.1$  mass % nickel. If the nickel concentration is higher or lower (minimum concentration that can be used is  $2.5 \pm 0.1$  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 ( $\geq 2.5 \pm 0.1$  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  $5.0 \pm 0.1$  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 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  $8.0 \pm 0.1$  mass % titanium or tin. If the titanium or tin concentration is higher or lower (minimum concentration that can be used is  $4.0 \pm 0.1$  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 ( $\geq 4.0 \pm 0.1$  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  $8.0 \pm 0.1$  mass % titanium or tin.

8.4.3 *Zirconium Octoate*, preferably containing  $12.0 \pm 0.1$  mass % zirconium. If the laboratory uses zirconium octoate with a lower mass % zirconium concentration level, the labo-

ratory needs to evaporate away the petroleum solvent to yield a solution that contains  $12.0 \pm 0.1$  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  $12.0 \pm 0.1$  mass % zirconium. If the zirconium concentration is  $< 12.0 \pm 0.1$  mass %, the laboratory needs to evaporate away the petroleum solvent to yield a solution that contains  $12.0 \pm 0.1$  mass % zirconium.

8.4.4 *Lead Naphthenate*, containing  $24.0 \pm 0.1$  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  $\geq 4$  mass % barium and certified to better than  $\pm 0.1$  % 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  $\geq 4$  mass % calcium and certified to better than  $\pm 0.1$  % 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  $\geq 4$  mass % phosphorus and certified to better than  $\pm 0.1$  % 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  $\geq 4$  mass % zinc and certified to better than  $\pm 0.1$  % 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  $\geq 2$  mass % sulfur and certified to better than  $\pm 0.1$  % 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  $240 \pm 0.5$  g of nickel octoate ( $5.0 \pm 0.1$  mass % nickel),  $30 \pm 0.1$  g of titanium 2-ethylhexoide ( $8.0 \pm 0.1$  mass % titanium) or  $30 \pm 0.1$  g of tin octoate ( $8.0 \pm 0.1$  mass % tin), and  $450 \pm 1$  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

<sup>4</sup> *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.

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  $1.000 \pm 0.001$  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  $1.000 \pm 0.001$  g of the internal standard solution described in 9.1 into a 30-mL bottle. Repeat for all of the calibration-standard bottles.

10.1.5 Add  $8.00 \pm 0.001$  g of each standard to a respective bottle containing the internal standards and shake or stir well (minimum of 10 min) to mix the constituents.

### 10.2 Sulfur:

10.2.1 Prepare five standards covering the range from 0.00 to 2.00 mass % sulfur in the diluent solvent.

10.2.2 Dispense  $1.000 \pm 0.001$  g of lead internal standard into 30-mL bottles (one bottle for each standard).

10.2.3 Add  $9.000 \pm 0.001$  g of each standard to each respective bottle containing internal standard. Shake or stir contents for a minimum of 10 min using apparatus defined in 6.2.

## 11. Instrument Calibration for Barium, Calcium, Phosphorus, Sulfur, and Zinc

11.1 Fill respective X-ray cups at least half full with the calibration standard solutions. Make sure that no wrinkles or bulges are present in the film. The film must be flat.

11.2 Place the sample cups in the X-ray beam in order to measure and record the net intensity (peak intensity—

background intensity) for both the analyte signal and the internal standard signal according to the wavelengths and conditions suggested in Table 3. Up to 60-s counting periods may be used at each wavelength position. Do this for each of the calibration standards for each of the elements.

NOTE 4—The parameters indicated in Table 3 are presented for guidance only and they will vary according to the instrument used.

11.3 Calculate the ratio, *R*, of the net element counts to their corresponding net internal standard counts for all of the net elements and standards as follows:

$$R = E/I \quad (4)$$

where:

- E* = net element counts, and
- I* = net internal standard counts.

NOTE 5—Many modern X-ray spectrometer instruments will calculate this ratio automatically and store the information in the instrument computer system.

11.4 Perform regression analyses for each calibration element by ratioing the net element counts to the net internal standard counts versus the element concentration (mass %) on linear graph paper or by way of the instrument computer system. It is recommended that two separate regression analyses be performed for each calibration set for barium, calcium, phosphorus, and zinc, as defined in 10.1.1 and 10.1.2. The regression analyses will determine a slope and intercept for each calibration element that will be used to determine element concentrations of samples to be tested.

## 12. Analysis of Quality Control Samples

12.1 A QC sample shall be analyzed each day samples are analyzed to verify the testing procedure and instrument performance. Additional QC samples may be analyzed. The QC samples shall be treated as outlined in Section 13.

## 13. Procedure

13.1 *Determination of Barium, Calcium, Phosphorus, and Zinc:*

TABLE 3 Suggested Parameters for Internal Standard Method

NOTE 1—These conditions serve as suggestions only. Optimum parameters may differ as a function of instrument, tube target, and crystal used. These conditions are for use with a chromium target and LiF<sub>200</sub> crystal.

	Line	Wavelength, Å	Angle, 2θ
Barium	<i>L</i> <sub>α<sub>1</sub></sub>	2.77596	87.17
Calcium	<i>K</i> <sub>α<sub>1,2</sub></sub>	3.35948	113.09
Tin (internal standard for barium)	<i>L</i> <sub>γ<sub>1</sub></sub>	3.00115	96.38
Tin (internal standard for calcium)	<i>L</i> <sub>α<sub>1</sub></sub>	3.5994	126.77
Titanium (alternative internal standard for barium and calcium)	<i>K</i> <sub>α<sub>1,2</sub></sub>	2.75216	86.23
Phosphorus	<i>K</i> <sub>α<sub>1,2</sub></sub>	2.836	89.56
Zirconium (internal standard for phosphorus)	<i>L</i> <sub>α<sub>1</sub></sub>	2.7958	87.96
Zinc	<i>K</i> <sub>α<sub>1,2</sub></sub>	1.43644	41.80
Nickel (internal standard for zinc)	<i>K</i> <sub>α<sub>1,2</sub></sub>	1.65791	48.63
Copper (alternative internal standard for zinc)	<i>K</i> <sub>α<sub>1,2</sub></sub>	1.54184	45.03
Sulfur	<i>K</i> <sub>α<sub>1,2</sub></sub>	2.4746	75.85
Lead (internal standard for sulfur)	<i>M</i> <sub>α<sub>1</sub></sub>	2.4345	74.41



13.1.1 If the concentration of the element is known or suspected to be less than 1.0 mass %, dispense  $8.000 \pm 0.001$  g of the sample specimen into a 30-mL bottle containing  $1.000 \pm 0.01$  g of internal standard solution 9.1 and  $1.000 \pm 0.001$  g of internal standard solution 9.2. Mix carefully using shaker for a minimum of 10 min.

13.1.2 If the concentration is known or found to be higher than 1.0 mass %, then dilute a sample specimen with the diluent solvent, such that the working concentration in the blend is reduced to approximately 0.5 mass %. Dispense  $8.000 \pm 0.001$  g of the *diluted* specimen into a 30-mL bottle containing  $1.000 \pm 0.001$  g of internal standard 9.1 and  $1.000 \pm 0.001$  g of internal standard 9.2. Mix carefully using shaker for a minimum of 10 min.

13.1.3 Pour a portion of sample from either 13.1.1 or 13.1.2 into a cell as described in 11.1 and obtain counts as described in 11.2. Calculate the ratio between the element and its internal standard as described in 11.3. Obtain the concentration of the element from the appropriate calibration curve. *Undiluted* sample results are to be reported *directly*.

NOTE 6—In addition to calibration standards identified in Section 10, 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.

13.1.4 The mass % of barium, calcium, phosphorus, or zinc, or a combination thereof, is calculated as follows:

$$\text{Element, mass \%} = M \frac{(S+D)}{S} \quad (5)$$

where:

$M$  = concentration of the element from the calibration curve, mass %,

$S$  = mass of sample specimen, g, and

$D$  = mass of diluent solvent, g.

### 13.2 Determination of Sulfur:

13.2.1 If the sulfur content is known to be less than 2 mass %, transfer a  $9.000 \pm 0.001$ -g sample specimen into a 30-mL bottle containing  $1.000 \pm 0.001$  g of the lead internal standard (9.2).

13.2.2 If the sulfur content is known or found to be higher than 2 mass %, dilute to approximately 1 to 1.5 mass % with the diluent solvent. Transfer  $9.000 \pm 0.001$  g of the diluted specimen into a 30-mL bottle containing  $1.000 \pm 0.001$  g of lead internal standard (9.2).

13.2.3 Run either 13.2.1 or 13.2.2 under the same conditions as the standards. Calculate the sulfur-to-lead ratio and obtain the sulfur concentration from the calibration curve. *Undiluted* sample results are reported directly. Refer to 13.1.4 for the calculation of *diluted* samples.

## TEST METHOD B (MATHEMATICAL CORRECTION PROCEDURE)

### 14. Reagents and Materials

14.1 *Helium*, for optical path of spectrometer.

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

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

### 14.4 Calibration Standard Materials<sup>4</sup>:

14.4.1 *Barium 2-Ethylhexoide*, with concentrations  $\geq 5$  mass % barium and certified to better than  $\pm 0.1$  % absolute, so that calibration standards can be prepared as stated in 15.1. Other barium containing organic matrices (free of other metals, sulfur, and phosphorus) may be used, provided the barium is stable in solution and the concentration is  $\geq 5$  mass % barium and certified to better than  $\pm 0.1$  % absolute (95 % confidence limit).

14.4.2 *Calcium Octoate*, with concentrations  $\geq 4$  mass % calcium and certified to better than  $\pm 0.1$  % absolute, so that calibration standards can be prepared as stated in 15.1. Other calcium containing organic matrices (free of other metals, sulfur, and phosphorus) may be used, provided the calcium is stable in solution and the concentration is  $\geq 4$  mass % calcium and certified to better than  $\pm 0.1$  % absolute (95 % confidence limit).

14.4.3 *Bis(2-Ethylhexyl)Hydrogen Phosphate*, 97 % purity (9.62 mass % phosphorus). Other phosphorus containing organic matrices (free of other metals and sulfur) may be substituted, provided the phosphorus is stable in solution and the concentration is  $\geq 2.5$  mass % phosphorus and certified to better than  $\pm 0.1$  % absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 15.1.

14.4.4 *Zinc Octoate*, with concentrations  $\geq 2.5$  mass % zinc and certified to better than  $\pm 0.1$  % absolute, so that calibration standards can be prepared as stated in 15.1. Other zinc containing organic matrices (free of other metals, sulfur, and phosphorus) may be used, provided the zinc is stable in solution, and the concentration is  $\geq 2.5$  mass % zinc and certified to better than  $\pm 0.1$  % absolute (95 % confidence limit).

14.4.5 *Di-n-Butyl Sulfide*, 97 % purity (21.9 mass % sulfur). Other sulfur containing organic matrices (free of metals and phosphorus) may be substituted, provided the sulfur is stable in solution and the concentration is  $\geq 7.5$  mass % sulfur and certified to better than  $\pm 0.1$  % absolute (95 % confidence limit), so that calibration standards can be prepared as stated in 15.1.

NOTE 7—Commercially available certified calibration blends may be used (see 8.5 and 14.4).

14.5 *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 18.

## 15. Preparation of Calibration Standards

15.1 Prepare calibration standards by precise dilution of each of the elements that meet the requirements of 14.4.1 to 14.4.5, with the diluent solvent for the recommended concentrations prescribed in Table 4.

15.2 Although Table 4 is an abbreviated listing of all the possible combinations of elements and concentration range interactions that can be tested to determine mathematical

**TABLE 4 Recommended Concentrations for Standards for the Mathematical Correction Procedure (All Values in Mass %)**

Standard	Barium	Calcium	Phosphorus	Sulfur	Zinc
1	0	0.80	0.5	0	0.5
2	1.0	0	0	0	0
3	1.0	0	0.5	0	0.5
4	0	0.80	0.5	1.5	0
5	0.5	0.40	0.25	0.75	0.25
6	0	0	0.5	1.5	0.5
7	1.0	0	0	1.5	0.5
8	1.0	0	0.5	1.5	0
9	0	0.80	0	1.5	0.5
10	0.5	0.40	0.25	0.75	0.25
11	1.0	0.80	0	1.5	0
12	1.0	0.80	0.5	1.5	0.5
13	0	0	0.5	0	0
14	0	0.80	0	0	0
15	0.5	0.40	0.25	0.75	0.25
16	1.0	0.80	0.5	0	0
17	0	0	0	1.5	0
18	0	0	0	0	0.5
19	1.0	0.80	0	0	0.5
20	0.5	0.40	0.25	0.75	0.25

correction factors for the various elements, the number of standards and the varying degree of element concentrations in the matrix are sufficient.

**16. Calibration**

16.1 Fill respective X-ray cups at least half full with the calibration standard solutions. Make sure that no wrinkles or bulges are present in the film. The film must be flat.

16.2 Place the sample cups in the X-ray beam in order to measure and record the net intensity (peak intensity—background intensity) for each element and in each calibration standard according to the wavelengths and conditions suggested in Table 5. Up to 60-s counting periods may be used at each wavelength position.

NOTE 8—The parameters indicated in Table 5 are presented for guidance only and they will vary according to the instrument used.

16.3 Interelement correction factors and the slope and intercept of the calibration line are obtained by the regression analysis using the program supplied with the particular instrument used (if available) or a model similar to the following form:

$$C_i = (D_i + E_i I_i) (1 + \sum_j \alpha_{ij} C_j) \tag{6}$$

**TABLE 5 Suggested Spectrometer Settings for Mathematical Correction Method**

	Barium	Calcium	Phosphorus	Sulfur	Zinc
Peak wavelength, Å	2.78	3.55	6.15	5.37	1.43
Analyzing crystal	LiF <sub>200</sub>	LiF <sub>200</sub>	germanium	graphite	LiF <sub>200</sub>
Peak angle, 2θ	87.13	113.1	140.92	106.22	41.79
Background angle, 2θ	85.7	114.5	142.90	108.00	43.6
Detector <sup>A</sup>	FS or D	F	F	F	FS or D

<sup>A</sup> F = flow proportional detector, S = scintillation detector, FS = both flow proportional and scintillation detectors, and D = use detector as recommended by manufacturer.

where:

- $C_i$  = concentration of the analyte Element  $i$ ,
- $D_i$  = intercept of the calibration curve for Element  $i$ ,
- $E_i$  = slope of the calibration curve for Element  $i$ ,
- $I_i$  = measured net intensity for Element  $i$ ,
- $\alpha_{ij}$  = interelement correction factor for effect of Element  $j$  on analyte Element  $i$ , and
- $C_j$  = concentration of interfering Element  $j$ .

A slope, intercept, and a set of interelement correction factors are calculated for each analyte.

16.4 The initial calibration to obtain the slope, intercept, and interelement correction factors is performed initially when the test method is set up, after any major maintenance is performed on the instrument that can affect the calibration (for example, new X-ray tube installed, new crystal added, and so forth), and as deemed necessary by the operator (for example, triggered by quality control sample results). Subsequent re-calibration is performed with a minimum of three standards containing each of the calibration elements at nominal concentrations across the respective calibration ranges in order to check the values of the slope and intercept. An optional stable pellet can also be prepared which can be measured on a periodic basis for the purpose of monitoring instrumental drift.

**17. Report**

17.1 Report the mass % element content to three significant digits (x.xx, 0.xxx, 0.0xxx).

17.2 State which test procedure was used.

**18. Analysis of Quality Control Samples**

18.1 A QC sample shall be analyzed each day samples are analyzed to verify the testing procedure and instrument performance. Additional QC samples may be analyzed. The QC samples shall be treated as outlined in Section 19.

**TABLE 6 Repeatability and Reproducibility**

Element	Repeatability	Reproducibility
	Internal Standard Procedure	
Barium	0.03214 X <sup>1.059</sup>	0.07105 X <sup>1.059</sup>
Calcium	0.0285 (X + 0.003) <sup>0.77</sup>	0.078 (X + 0.003) <sup>0.77</sup>
Phosphorus	0.0411 X <sup>0.756</sup>	0.078 X <sup>0.756</sup>
Sulfur	0.03966 X	0.2098 X
Zinc	0.0157 X <sup>0.83</sup>	0.0373 X <sup>0.83</sup>
Mathematical Correction Procedure		
Barium	0.02028 X	0.1593 X
Calcium	0.018 X <sup>0.71</sup>	0.07841 X <sup>0.71</sup>
Phosphorus	0.033 X <sup>0.812</sup>	0.1138 X <sup>0.812</sup>
Sulfur	0.05335 (X + 0.001)	0.1669 (X + 0.001)
Zinc	0.0197 (X + 0.001) <sup>1.114</sup>	0.1206 (X + 0.001) <sup>1.114</sup>

**19. Procedure**

19.1 Fill X-ray cups at least half full with the sample specimens to be analyzed. Make sure that no wrinkles or bulges exist in the film. The film must be flat.

19.2 Obtain intensities for all of the elements for all of the samples in the manner prescribed for the standards (16.2).