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An American National Standard

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 D 4927; 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 1-11, and 17).

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 12-17).

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.*

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance[2]

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

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

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[2] *Annual Book of ASTM Standards*, Vol 05.03.

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

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 polyethylene terephthalate (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 9.1.1 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 9.1.1 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 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 9.1.1

[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.

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 9.1.1 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% relative, 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 % relative, 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 % relative, 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 % relative, 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% relative, 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*:

9.1.1 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:

$$A = 240 \times (5/x) \tag{1}$$

$$B = 30 \times (8/y) \tag{2}$$

$$C = 720 - [A + B] \tag{3}$$

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*:

9.2.1 *Lead Naphthenate* (**Warning—**Hazardous. Lead naphthenate is toxic and precautions should be taken to avoid inhalation of vapors, ingestion, or skin contact.) 24 mass % lead, serves as a suitable internal standard. 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 7.4.3 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 8.1.1 into a 30-mL bottle. Repeat for all of the calibration-standard bottles.

10.1.5 Add 8.00 ± 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 ± 0.001 g of lead internal standard into 30-mL bottles (one bottle for each standard).

10.2.3 Add 9.000 ± 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 2. 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 2 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:

$$R = E/I \tag{4}$$

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.

TABLE 2 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_{200} crystal.

	Line	Wavelength, Å	Angle, 2θ
Barium	$L\alpha_1$	2.77596	87.17
Calcium	$K\alpha_{1,2}$	3.35948	113.09
Tin (internal standard for barium)	$L_{\gamma1}$	3.00115	96.38
Tin (internal standard for calcium)	$L\alpha_1$	3.5994	126.77
Titanium (alternative internal standard for barium and calcium) $K\alpha_2$	2.75216	86.23	
Phosphorus	$K\alpha_{1,2}$	2.836	89.56
Zirconium (internal standard for phosphorus)	$L\alpha_1$	2.7958	87.96
Zinc	$K\alpha_{1,2}$	1.43644	41.80
Nickel (internal standard for zinc)	$K\alpha_{1,2}$	1.65791	48.63
Copper (alternative internal standard for zinc)	$K\alpha_{1,2}$	1.54184	45.03
Sulfur	$K\alpha_{1,2}$	2.4746	75.85
Lead (internal standard for sulfur)	$M\alpha_1$	2.4345	74.41

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*:

13.1.1 If the concentration of the element is known or suspected to be less than 1.0 mass %, dispense 8.000 ± 0.001 g of the sample specimen into a 30-mL bottle containing 1.000 ± 0.01 g of internal standard solution 9.1.1 and 1.000 ± 0.001 of internal standard solution 8.1.2. 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 ± 0.001 g of the *diluted* specimen into a 30-mL bottle containing 1.000 ± 0.001 g of internal standard 9.1.1 and 1.000 ± 0.001 g of internal standard 8.1.2. 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 14.4.1-14.4.5, 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.

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

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

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 ± 0.001-g sample specimen into a 30-mL bottle containing 1.000 ± 0.001 g of the lead internal standard (9.2.1).

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 ± 0.001 g of the diluted specimen into a 30-mL bottle containing 1.000 ± 0.001 g of lead internal standard (9.2.1).

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*[4]:

14.4.1 *Barium 2-Ethylhexoide*, with concentrations ≥5 mass % barium and certified to better than ±0.1 % relative, 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 ≥5 mass % barium and certified to better than ±0.1 % relative.

14.4.2 *Calcium Octoate*, with concentrations ≥4 mass % calcium and certified to better than ±0.1 % relative, 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 ≥4 mass % calcium and certified to better than ±0.1 % relative.

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 ≥2.5 mass % phosphorus and certified to better than ±0.1 % relative, so that calibration standards can be prepared as stated in 15.1.

14.4.4 *Zinc Octoate*, with concentrations ≥2.5 mass % zinc and certified to better than ±0.1 % relative, 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 ≥2.5 mass % zinc and certified to better than ±0.1 % relative.

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 ≥7.5 mass % sulfur and certified to better than ±0.1 % relative, so that calibration standards can be prepared as stated in 15.1.

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 3.

15.2 Although Table 3 is an abbreviated listing of all the possible combinations of elements and concentration range interactions that can be tested to determine mathematical 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 4. Up to 60-s counting periods may be used at each wavelength position.

NOTE 7—The parameters indicated in Table 4 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:

TABLE 3 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

TABLE 4 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_{200}	LiF_{200}	germanium	graphite	LiF_{200}
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[A]	*FS*	*F*	*F*	*F*	*FS*

[A] *F* = flow proportional detector, *S* = scintillation detector, and *FS* = both detectors.

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

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*,
α_{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.

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).

19.3 The elemental concentrations for each sample specimen are calculated using the measured intensities combined with the correction factors obtained from the calibration procedure (16.3).

TABLE 5 Repeatability and Reproducibility

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

19.4 Procedures 19.1 to 19.3 are repeated on diluted sample specimens in those cases where elemental concentrations exceed 1 mass % for barium, calcium, phosphorus, or zinc, or 2 mass % for sulfur.

20. Quality Control

20.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample (Section 12 for test method A or Section 18 for test method B).

20.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

20.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

21. Precision and Bias [5]

21.1 The precision of these test methods as determined by the statistical examination of the interlaboratory test results is as follows:

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

21.1.1.1 *Test Method A*—Values can be obtained for each element for any given concentration within the scope of this test method by using the expressions listed in Table 5 or the curves shown in Fig. 1.

21.1.1.2 *Test Method B*—Values can be obtained for each element for any given concentration within the scope of this test method by using the expressions listed in Table 5 or the curves shown in Fig. 1.

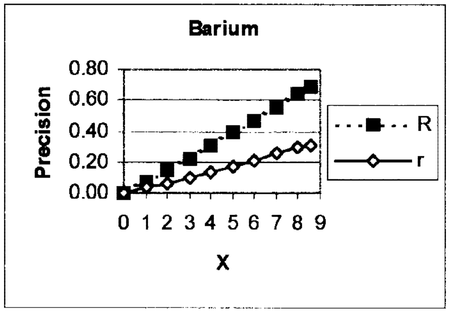
21.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following values only in one case in twenty.

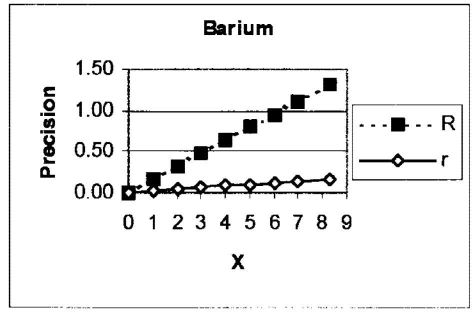
21.1.2.1 *Test Method A*—Values can be obtained for each element for any given concentration within the scope of this

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1259.

Internal Standard: Barium

X	r	R
0.038120	0.0010	0.0022
1	0.0321	0.0711
2	0.0670	0.1480
3	0.1029	0.2274
4	0.1395	0.3084
5	0.1767	0.3906
6	0.2143	0.4738
7	0.2524	0.5579
8	0.2907	0.6426
9	0.3111	0.6878



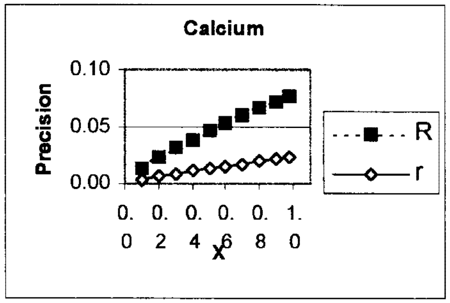


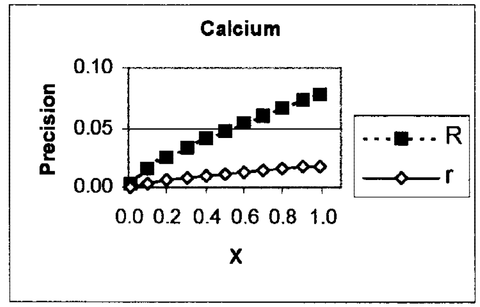
Mathematical Correction: Barium

X	r	R
0.03828	0.0008	0.0061
1	0.0203	0.1593
2	0.0406	0.3186
3	0.0608	0.4779
4	0.0811	0.6372
5	0.1014	0.7965
6	0.1217	0.9558
7	0.1420	1.1151
8.3142	0.1686	1.3245

Internal Standard: Calcium

X	r	R
0.10222	0.0041	0.0138
0.2	0.0067	0.0228
0.3	0.0092	0.0311
0.4	0.0114	0.0387
0.5	0.0135	0.0460
0.6	0.0155	0.0528
0.7	0.0174	0.0595
0.8	0.0193	0.0659
0.9	0.0211	0.0721
0.97734	0.0225	0.0768



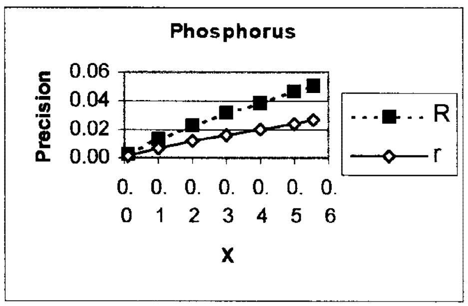


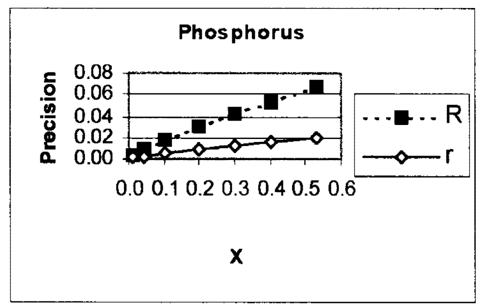
Mathematical Correction: Calcium

X	r	R
0.00913	0.0006	0.0028
0.1	0.0035	0.0153
0.2	0.0057	0.0250
0.3	0.0077	0.0333
0.4	0.0094	0.0409
0.5	0.0110	0.0479
0.6	0.0125	0.0546
0.7	0.0140	0.0609
0.8	0.0154	0.0669
0.9	0.0167	0.0727
0.98927	0.0179	0.0778

Internal Standard: Phosphorus

X	r	R
0.012227	0.0015	0.0028
0.1	0.0072	0.0137
0.2	0.0122	0.0231
0.3	0.0165	0.0314
0.4	0.0205	0.0390
0.5	0.0243	0.0462
0.55752	0.0264	0.0501





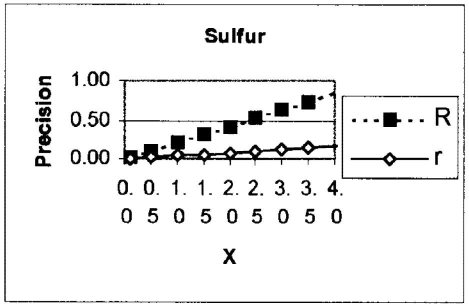
Mathematical Correction: Phosphorus

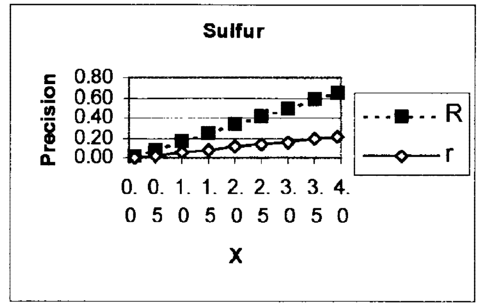
X	r	R
0.01204	0.0009	0.0031
0.04125	0.0025	0.0085
0.1	0.0051	0.0175
0.2	0.0089	0.0308
0.3	0.0124	0.0428
0.4	0.0157	0.0541
0.53246	0.0198	0.0682

FIG. 1 Repeatability, r, and Reproducibility, R, at Selected Values

Internal Standard: Sulfur

X	r	R
0.12333	0.0049	0.0259
0.5	0.0198	0.1049
1.0	0.0397	0.2098
1.5	0.0595	0.3147
2.0	0.0793	0.4196
2.5	0.0992	0.5245
3.0	0.1190	0.6294
3.5	0.1388	0.7343
4.0	0.1599	0.8458



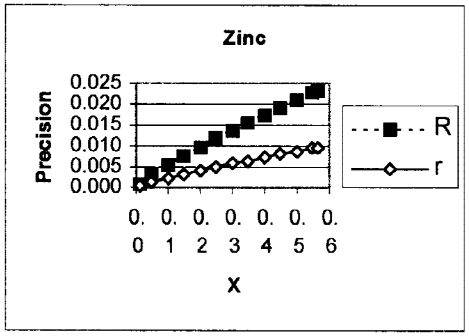


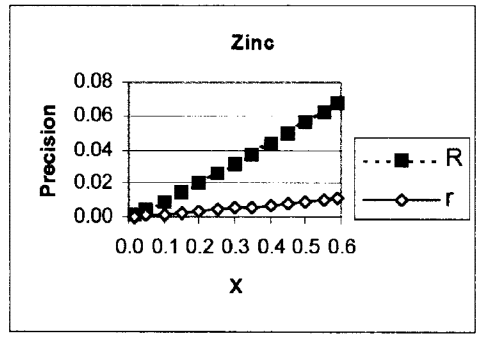
Mathematical Correction: Sulfur

X	r	R
0.11641	0.0063	0.0196
0.5	0.0267	0.0836
1.0	0.0534	0.1671
1.5	0.0801	0.2505
2.0	0.1068	0.3340
2.5	0.1334	0.4174
3.0	0.1601	0.5009
3.5	0.1868	0.5843
3.9118	0.2087	0.6530

Internal Standard: Zinc

X	r	R
0.013664	0.0004	0.0010
0.05	0.0013	0.0031
0.10	0.0023	0.0055
0.15	0.0032	0.0077
0.20	0.0041	0.0098
0.25	0.0050	0.0118
0.30	0.0058	0.0137
0.35	0.0066	0.0156
0.40	0.0073	0.0174
0.45	0.0081	0.0192
0.50	0.0088	0.0209
0.55	0.0096	0.0227
0.56294	0.0098	0.0231





Mathematical Correction: Zinc

X	r	R
0.01344	0.0002	0.0011
0.05	0.0007	0.0044
0.10	0.0015	0.0094
0.15	0.0024	0.0147
0.20	0.0033	0.0202
0.25	0.0042	0.0259
0.30	0.0052	0.0317
0.35	0.0061	0.0376
0.40	0.0071	0.0436
0.45	0.0081	0.0497
0.50	0.0091	0.0558
0.55	0.0101	0.0621
0.59	0.0110	0.0671

FIG. 1 Repeatability, r, and Reproducibility, R, at Selected Values *(continued)*

test method by using the expressions listed in Table 5 or the curves shown in Fig. 1.

21.1.2.2 *Test Method B*—Values can be obtained for each element for any given concentration within the scope of this test method by using the expressions listed in Table 5 or the curves shown in Fig. 1.

21.2 *Bias*—The bias for these test methods was not determined since no suitable reference materials of known composition were available.

22. Keywords

22.1 additives; barium; calcium; lubricating oil; phosphorous; sulfur; wavelength-dispersive; X-ray fluorescence; zinc

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practice D 6299 and *ASTM MNL 7*[6]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D 6299 and *ASTM MNL 7*). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM method precision to ensure data quality.

X1.5 It is recommended then, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X1.6 See Practice D 6299 and *ASTM MNL 7* for further guidance on QC and Control Charting techniques.

[6] *ASTM MNL 7*, “Manual on Presentation of Data Control Chart Analysis,” 6th ed., ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 4927 – 01) that may impact the use of this standard.

(1) Updated 1.1, added a new Table 1, and renumbered subsequent tables.
(2) Updated section references in 1.2 and 1.3.
(3) Added a new Section 17, Report.
(4) Removed Tables 5 and 6 (as renumbered for the insertion of the new Table 1) and replaced with a new Table 5.
(5) Added a new Fig. 1 and included references to Fig. 1 in Sections 21.1.1.1, 21.1.1.2, 21.1.2.1, and 21.1.2.2.