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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 has been approved for use by agencies of the U.S. Department of Defense.

1. ~~Scope~~ 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

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,

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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

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~~absorption 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)~~ 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~~test specimen is placed in the X-ray ~~beam and the intensities of the fluorescence lines of~~beam. Total net counts or intensities (peak intensity – background) for 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.~~ measured at their appropriate wavelengths. Concentrations of the elements of interest are determined by comparison of net signals against ~~appropriate interelement correction factors~~calibration curves developed from responses of calibration standards. The calibration procedure includes interelement corrections.

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

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

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.~~ element; this is further referred to as "enhancement." These effects are significant at concentrations varying from 0.03 % by mass due to the heavier elements to 1 % by mass for the lighter elements. The measured intensity for a given element can be mathematically corrected for the absorption and enhancement 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 *Wavelength Dispersive X-Ray Spectrometer,* equipped for ~~soft X-ray~~ detection of ~~radiation~~ soft X-ray in the range from ~~1~~ 0.1 nm to 1.0 nm (1 A˚ to ~~10~~ 10 A˚.). 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~~(LiF200)~~,~~$_{200}$), 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 mil to 0.35 mil (6.3 μm 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.

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[3] A registered trademark of ~~E. I. du Pont de Nemours and Co.~~DuPont Teijin Films, LP.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

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 % by volume argon and 10 % by volume methane for the flow proportional counter.

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

8.4 *Internal Standard Materials:*

8.4.1 *Nickel Octoate,* preferably containing 5.0 % by mass ± 0.1 % by mass nickel. If the nickel concentration is higher or lower (minimum concentration that can be used is 2.5 % by mass ± 0.1 % by 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 % by mass ± 0.1 % by 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 % by mass ± 0.1 % by 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. The use of a primary beam filter (such as, for example, 100 micron Al) when measuring Cu is recommended to fully avoid problems with the tube contamination.

8.4.2 *Titanium 2-Ethylhexoide or Tin Octoate,* preferably containing 8.0 % by mass ± 0.1 % by mass titanium or tin. If the titanium or tin concentration is higher or lower (minimum concentration that can be used is 4.0 % by mass ± 0.1 % by 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 % by mass ± 0.1 % by 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 % by mass ± 0.1 % by mass titanium or tin.

8.4.3 *Zirconium Octoate,* preferably containing 12.0 % by mass ± 0.1 % by 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 % by mass ± 0.1 % by 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 % by mass ± 0.1 % by mass zirconium. If the zirconium concentration is <12.0 % by mass ± 0.1 % by mass, the laboratory needs to evaporate away the petroleum solvent to yield a solution that contains 12.0 % by mass ± 0.1 % by mass zirconium.

8.4.4 *Lead Naphthenate,* containing 24.0 % by mass ± 0.1 % by 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 percent levels.

8.5.1 *Barium 2-Ethylhexoide or Sulfonate,* with concentrations ≥4 % by 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 % by 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 % by 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 % ≥4 % by 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 % ≥4 % by 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 % by 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 % by 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 g ± 0.5 g of nickel octoate (5.0 % ± 0.1 % by mass nickel), 30 g ± 0.1 g of titanium 2-ethylhexoide (8.0 % ± 0.1 % by mass titanium) or 30 g ± 0.1 g of tin octoate (8.0 % ± 0.1 % by mass tin), and 450 g ± 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*—Lead naphthenate, 24 % by 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 % by mass, prepare standards containing 0.00 % by mass, 0.01 % by mass, 0.025 % by mass, 0.050 % by mass, 0.075 % by mass, and 0.10 % by mass of each respective element in the diluent solvent.

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

10.1.3 Dispense 1.000 g ± 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 g ± 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 g ± 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 % by mass to 2.00 % by mass sulfur in the diluent solvent.

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

10.2.3 Add 9.000 g ± 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 minus background~~ intensity) for both the analyte signal and the internal standard ~~signal according~~signal. Table 3 ~~to the wavelengths and conditions suggested in~~ provides suggested crystal parameters. ~~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:

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

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.

Note 6—Many modern X-ray spectrometer instruments use count rate (intensity, expressed in kcps) instead of counts collected in a given measuring time.

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~~ Following apparatus supplier guidance, the measurement of net ~~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.~~element counts and net internal standards counts shall include background correction.

11.4.1 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$_{200}$ crystal.

	Line	Wavelength, Å	Angle, 2θ
Barium	Lα$_1$	2.77596	87.17
Calcium	Kα$_{1,2}$	3.35948	113.09
Tin (internal standard for barium)	Lγ$_1$	3.00115	96.38
Tin (internal standard for calcium)	Lα$_1$	3.5994	126.77
Titanium (alternative internal standard for barium and calcium)	Kα$_{1,2}$	2.75216	86.23
Phosphorus	Kα$_{1,2}$	2.836	89.56
Zirconium (internal standard for phosphorus)	Lα$_1$	2.7958	87.96
Zinc	Kα$_{1,2}$	1.43644	41.80
Nickel (internal standard for zinc)	Kα$_{1,2}$	1.65791	48.63
Copper (alternative internal standard for zinc)	Kα$_{1,2}$	1.54184	45.03
Sulfur	Kα$_{1,2}$	2.4746	75.85
Lead (internal standard for sulfur)	Mα$_1$	2.4345	74.41

TABLE 3 Suggested Parameters for Internal Standard Method

	Line designation IUPAC (Siegbahn)	Peak Wavelength (nm)	Crystal	Peak Angle (2θ)	Background Angle (2θ)	Detector[A]
Barium	L$_3$-M$_5$ (Lα$_1$)	0.27759	LiF200	87.17	85.70	F
Calcium	K-L$_{2,3}$ (Kα$_{1,2}$)	0.33595	LiF200	113.09	114.5	F
Titanium (internal standard for barium and calcium)	K-L$_{2,3}$ (Kα$_{1,2}$)	0.2752	LiF200	86.23	(85.70)[B]	F
Tin (internal standard for barium)	L$_2$-N$_4$ (Lγ$_1$)	0.30012	LiF200	96.38	(85.70)	F
Tin (internal standard for calcium)	L$_3$-M$_5$ (Lα$_1$)	0.35994	LiF200	86.23	(114.5)	F
Phosphorus	K-L$_{2,3}$ (Kα$_{1,2}$)	0.615	PET	89.56	90.24	F
Zirconium (internal standard for phosphorus)	L$_3$-M$_5$ (Lα$_1$)	0.6071	PET	87.96	(90.24)	F
Phosphorus (recommended)[C]	K-L$_{2,3}$ (Kα$_{1,2}$)	0.615	Ge	140.92	142.90	F
Zirconium (internal standard for calcium) (recommended)	L$_3$-M$_5$ (Lα$_1$)	0.6071	Ge	136.96	(142.90)	F
Sulfur	K-L$_{2,3}$ (Kα$_{1,2}$)	0.537	PET	75.8	76.8	F
Lead (internal standard for sulfur)	M$_5$-N$_7$ (Mα$_1$)	0.5254	PET	74.4	(76.8)	F
Sulfur (recommended)	K-L$_{2,3}$ (Kα$_{1,2}$)	0.537	Ge	110.24	112.69	F
Lead (internal standard for sulfur) (recommended)	M$_5$-N$_7$ (Mα$_1$)	0.5254	Ge	107.24	(112.69)	F
Zinc	K-L$_{2,3}$ (Kα$_{1,2}$)	0.143	LiF200	41.79	43.6	FS or D
Nickel (internal standard for zinc)	K-L$_{2,3}$ (Kα$_{1,2}$)	0.16579	LiF200	48.63	(43.6)	FS or D
Copper (alternative internal standard for zinc)	K-L$_{2,3}$ (Kα$_{1,2}$)	0.15418	LiF200	45.03	(43.6)	FS or D

[A] F = flow proportional detector, S = scintillation detector, FS = both flow proportional and scintillation detectors, and D = use detector as recommended by manufacturer.
[B] Values between brackets are the same background positions as for the analyte peak.
[C] The use of Ge is recommended.

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

13.1.2 If the mass fraction of the element is known or found to be higher than 1.0 %, then dilute a sample specimen with the diluent solvent, such that the working mass fraction in the blend is reduced to approximately 0.5 %. Dispense 8.000 g ± 0.001 g of the *diluted* specimen into a 30 mL bottle containing 1.000 g ± 0.001 g of internal standard solution 9.1 and 1.000 g ± 0.001 g of the zirconium internal standard. Mix carefully using a 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 7—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.