



Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)¹

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

^{ε1} NOTE—Equation 9 and Paragraph 8.3 were corrected editorially in November 2003.

INTRODUCTION

Costs associated with maintenance due to engine and machine wear can be significant. Therefore, diagnostic methods for determining the condition of engines and other machinery can be important. This test method is intended to quantify, for the purpose of equipment monitoring, the concentration of metals in used lubricating oils. Although the precision statement was determined by analyzing a variety of used oils this test method can, in principle, be used for the analysis of unused oils to provide more complete elemental composition data than Test Methods D 4628, D 4927 or D 4951.

1. Scope*

1.1 This test method covers the determination of additive elements, wear metals, and contaminants in used lubricating oils by inductively coupled plasma atomic emission spectrometry (ICP-AES). The specific elements are listed in Table 1.

1.2 This test method covers the determination of selected elements, listed in Table 1, in re-refined and virgin base oils.

1.3 For analysis of any element using wavelengths below 190 nm, a vacuum or inert-gas optical path is required. The determination of sodium and potassium is not possible on some instruments having a limited spectral range.

1.4 This test method uses oil-soluble metals for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent, and low results are obtained for particles larger than a few micrometers.²

1.5 Elements present at concentrations above the upper limit of the calibration curves can be determined with additional, appropriate dilutions and with no degradation of precision.

1.6 For elements other than calcium, sulfur, and zinc, the low limits listed in Table 2 and Table 3 were estimated to be ten

times the repeatability standard deviation. For calcium, sulfur, and zinc, the low limits represent the lowest concentrations tested in the interlaboratory study.

1.7 The values stated in SI (metric) units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.8 *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.* Specific precautionary statements are given in 6.1, 8.2, and 8.4.

2. Referenced Documents

2.1 ASTM Standards:

C 1109 Test Method for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectrometry³

D 1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)⁴

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁵

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards⁵

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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² Eisentraut, K. J., Newman, R. W., Saba, C. S., Kauffman, R. E., and Rhine, W. E., *Analytical Chemistry*, Vol 56, 1984.

³ *Annual Book of ASTM Standards*, Vol 12.01.

⁴ *Annual Book of ASTM Standards*, Vol 05.01.

⁵ *Annual Book of ASTM Standards*, Vol 05.02.

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

TABLE 1 Elements Determined and Suggested Wavelengths^A

| Element | Wavelength, nm |
|------------|--|
| Aluminum | 308.22, 396.15, 309.27 |
| Barium | 233.53, 455.40, 493.41 |
| Boron | 249.77 |
| Calcium | 315.89, 317.93, 364.44, 422.67 |
| Chromium | 205.55, 267.72 |
| Copper | 324.75 |
| Iron | 259.94, 238.20 |
| Lead | 220.35 |
| Magnesium | 279.08, 279.55, 285.21 |
| Manganese | 257.61, 293.31, 293.93 |
| Molybdenum | 202.03, 281.62 |
| Nickel | 231.60, 277.02, 221.65 |
| Phosphorus | 177.51, 178.29, 213.62, 214.91, 253.40 |
| Potassium | 766.49 |
| Sodium | 589.59 |
| Silicon | 288.16, 251.61 |
| Silver | 328.07 |
| Sulfur | 180.73, 182.04, 182.62 |
| Tin | 189.99, 242.95 |
| Titanium | 337.28, 350.50, 334.94 |
| Vanadium | 292.40, 309.31, 310.23, 311.07 |
| Zinc | 202.55, 206.20, 313.86, 334.58, 481.05 |

^A These wavelengths are only suggested and do not represent all possible choices.

TABLE 2 Repeatability

| Element | Range, mg/kg | Repeatability, $\mu\text{g/g}^A$ |
|------------|--------------|----------------------------------|
| Aluminum | 6–40 | 0.71 $X^{0.41}$ |
| Barium | 0.5–4 | 0.24 $X^{0.66}$ |
| Boron | 4–30 | 0.26 X |
| Calcium | 40–9000 | 0.0020 $X^{1.4}$ |
| Chromium | 1–40 | 0.17 $X^{0.75}$ |
| Copper | 2–160 | 0.12 $X^{0.91}$ |
| Iron | 2–140 | 0.13 $X^{0.80}$ |
| Lead | 10–160 | 1.6 $X^{0.32}$ |
| Magnesium | 5–1700 | 0.16 $X^{0.86}$ |
| Manganese | 5–700 | 0.010 $X^{1.3}$ |
| Molybdenum | 5–200 | 0.29 $X^{0.70}$ |
| Nickel | 5–40 | 0.52 $X^{0.49}$ |
| Phosphorus | 10–1000 | 1.3 $X^{0.58}$ |
| Potassium | 40–1200 | 3.8 $X^{0.33}$ |
| Silicon | 8–50 | 1.3 $X^{0.26}$ |
| Silver | 0.5–50 | 0.15 $X^{0.83}$ |
| Sodium | 7–70 | 0.49 $X^{0.66}$ |
| Sulfur | 900–6000 | 0.49 $X^{0.81}$ |
| Tin | 10–40 | 2.4 $X^{0.17}$ |
| Titanium | 5–40 | 0.54 $X^{0.37}$ |
| Vanadium | 1–50 | 0.061 X |
| Zinc | 60–1600 | 0.15 $X^{0.88}$ |

^A Where: X = mean concentration, $\mu\text{g/g}$.

D 4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry⁵

D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectrometry⁵

D 4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry⁵

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁶

TABLE 3 Reproducibility

| Element | Range, mg/kg | Reproducibility, $\mu\text{g/g}^A$ |
|------------|--------------|------------------------------------|
| Aluminum | 6–40 | 3.8 $X^{0.26}$ |
| Barium | 0.5–4 | 0.59 $X^{0.92}$ |
| Boron | 4–30 | 13 $X^{0.01}$ |
| Calcium | 40–9000 | 0.015 $X^{1.3}$ |
| Chromium | 1–40 | 0.81 $X^{0.61}$ |
| Copper | 2–160 | 0.24 X |
| Iron | 2–140 | 0.52 $X^{0.80}$ |
| Lead | 10–160 | 3.0 $X^{0.36}$ |
| Magnesium | 5–1700 | 0.72 $X^{0.77}$ |
| Manganese | 5–700 | 0.13 $X^{1.2}$ |
| Molybdenum | 5–200 | 0.64 $X^{0.71}$ |
| Nickel | 5–40 | 1.5 $X^{0.50}$ |
| Phosphorus | 10–1000 | 4.3 $X^{0.50}$ |
| Potassium | 40–1200 | 6.6 $X^{0.29}$ |
| Silicon | 8–50 | 2.9 $X^{0.39}$ |
| Silver | 5–50 | 0.35 X |
| Sodium | 7–70 | 1.1 $X^{0.71}$ |
| Sulfur | 900–6000 | 1.2 $X^{0.75}$ |
| Tin | 10–40 | 2.1 $X^{0.62}$ |
| Titanium | 5–40 | 2.5 $X^{0.47}$ |
| Vanadium | 1–50 | 0.28 $X^{1.1}$ |
| Zinc | 60–1600 | 0.083 $X^{1.1}$ |

^A Where: X = mean concentration, $\mu\text{g/g}$.

3. Terminology

3.1 Definitions:

3.1.1 *emission spectroscopy*—refer to Terminology E 135.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *additive element*—a constituent of a chemical compound that improves the performance of a lubricating oil.

3.2.2 *analyte*—an element whose concentration is being determined.

3.2.3 *Babington-type nebulizer*—a device that generates an aerosol by flowing a liquid over a surface that contains an orifice from which gas flows at a high velocity.

3.2.4 *calibration*—the process by which the relationship between signal intensity and elemental concentration is determined for a specific element analysis.

3.2.5 *calibration curve*—the plot of signal intensity versus elemental concentration using data obtained by making measurements with standards.

3.2.6 *contaminant*—a foreign substance, generally undesirable, introduced into a lubricating oil.

3.2.7 *detection limit*—the concentration of an analyte that results in a signal intensity that is some multiple (typically two) times the standard deviation of the background intensity at the measurement wavelength.

3.2.8 *inductively-coupled plasma (ICP)*—a high-temperature discharge generated by flowing an ionizable gas through a magnetic field induced by a load coil that surrounds the tubes carrying the gas.

3.2.9 *linear response range*—the elemental concentration range over which the calibration curve is a straight line, within the precision of the test method.

3.2.10 *profiling*—a technique that determines the wavelength for which the signal intensity measured for a particular analyte is a maximum.

3.2.11 *radio frequency (RF)*—the range of frequencies between the audio and infrared ranges (3 kHz to 300 GHz).

3.2.12 *wear metal*—an element introduced into the oil by wear of oil-wetted parts.

⁶ Annual Book of ASTM Standards, Vol 03.05.

4. Summary of Test Method

4.1 A weighed portion of a thoroughly homogenized used oil is diluted ten-fold by weight with mixed xylenes or other suitable solvent. Standards are prepared in the same manner. An optional internal standard can be added to the solutions to compensate for variations in test specimen introduction efficiency. The solutions are introduced to the ICP instrument by free aspiration or an optional peristaltic pump. By comparing emission intensities of elements in the test specimen with emission intensities measured with the standards, the concentrations of elements in the test specimen are calculable.

5. Significance and Use

5.1 This test method covers the rapid determination of 22 elements in used lubricating oils and in base oils, and it provides rapid screening of used oils for indications of wear. Test times approximate a few minutes per test specimen, and detectability for most elements is in the low mg/kg range. In addition, this test method covers a wide variety of metals in virgin and re-refined base oils. Twenty-two elements can be determined rapidly, with test times approximating several minutes per test specimen.

5.2 When the predominant source of additive elements in used lubricating oils is the additive package, significant differences between the concentrations of the additive elements and their respective specifications can indicate that the incorrect oil is being used. The concentrations of wear metals can be indicative of abnormal wear if there are baseline concentration data for comparison. A marked increase in boron, sodium, or potassium levels can be indicative of contamination as a result of coolant leakage in the equipment. This test method can be used to monitor equipment condition and define when corrective actions are needed.

5.3 The concentrations of metals in re-refined base oils can be indicative of the efficiency of the re-refining process. This test method can be used to determine if the base oil meets specifications with respect to metal content.

6. Interferences

6.1 *Spectral*—Check all spectral interferences expected from the elements listed in Table 1. Follow the manufacturer's operating guide to develop and apply correction factors to compensate for the interferences. To apply interference corrections, all concentrations must be within the previously established linear response range of each element listed in Table 1. (**Warning**—Correct profiling is important to reveal spectral interferences from high concentrations of additive elements on the spectral lines used for determining wear metals.)

6.1.1 Spectral interferences can usually be avoided by judicious choice of analytical wavelengths. When spectral interferences cannot be avoided, the necessary corrections should be made using the computer software supplied by the instrument manufacturer or the empirical method described below. Details of the empirical method are given in Test

Method C 1109 and by Boumans.⁷ This empirical correction method cannot be used with scanning spectrometer systems when both the analytical and interfering lines cannot be located precisely and reproducibly. With any instrument, the analyst must always be alert to the possible presence of unexpected elements producing interfering spectral lines.

6.1.2 The empirical method of spectral interference correction uses interference correction factors. These factors are determined by analyzing the single-element, high-purity solutions under conditions matching as closely as possible those used for test specimen analysis. Unless plasma conditions can be accurately reproduced from day to day, or for longer periods, interference correction factors found to affect the results significantly must be redetermined each time specimens are analyzed.

6.1.3 Interference correction factors, K_{ia} , are defined as follows: For analyte a , we have:

$$Ca = Ia/Ha \quad (1)$$

where:

- Ca = concentration of analyte a ,
- Ia = net line intensity (that is, background corrected) of analyte a , and
- Ha = sensitivity.

6.1.3.1 Similarly, for an interferent i at the same wavelength:

$$Ci = Ii/Hi \quad (2)$$

where:

- Ii = contribution from the peak or wing of the interferent line to the peak intensity of the analyte a .

6.1.3.2 The correction factor, K_{ia} is defined as:

$$K_{ia} = Hi/Ha = Ii/(Ci \times Ha) \quad (3)$$

6.1.3.3 Analysis of high-purity stock solutions with a calibrated instrument gives Ii/Ha , the concentration error that results when analyzing a solution containing an interferent of concentration Ci . Dividing by Ci gives the dimensionless correction factor K_{ia} . To apply these correction factors:

$$Ca, \text{ apparent} = (Ia + Ii)/Ha \quad (4)$$

$$Ca, \text{ apparent} = Ca + Ii/Ha \quad (5)$$

$$Ca = Ca, \text{ apparent} - Ii/Ha \quad (6)$$

$$Ca = Ca, \text{ apparent} - K_{ia} * Ci \quad (7)$$

and, for more than one interferent:

$$Ca = Ca, \text{ apparent} - K_{1a} \times C1 - K_{2a} \times C2 - \dots \quad (8)$$

6.1.4 Interference correction factors can be negative if off-peak background correction is employed for element i . A negative K_{ia} can result when an interfering line is encountered at the background correction wavelength rather than at the peak wavelength.

⁷ Boumans, P. W. J. M., "Corrections for Spectral Interferences in Optical Emission Spectrometry with Special Reference to the RF Inductively Coupled Plasma," *Spectrochimica Acta*, 1976, Vol 31B, pp. 147–152.

6.2 *Viscosity Effects*—Differences in the viscosities of test specimen solutions and standard solutions can cause differences in the uptake rates. These differences can adversely affect the accuracy of the analysis. The effects can be reduced by using a peristaltic pump to deliver solutions to the nebulizer or by the use of internal standardization, or both. When severe viscosity effects are encountered, dilute the test specimen and standard 20-fold rather than 10-fold while maintaining the same concentration of the internal standard.

6.3 *Particulates*—Particulates can plug the nebulizer thereby causing low results. Use of a Babington type high-solids nebulizer helps to minimize this effect. Also, the specimen introduction system can limit the transport of particulates, and the plasma can incompletely atomize particulates, thereby causing low results.

7. Apparatus

7.1 *Balance*, top loading, with automatic tare, capable of weighing to 0.001 g, capacity of 150 g.

7.2 *Inductively-Coupled Plasma Atomic Emission Spectrometer*—Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz ICP torch and RF generator to form and sustain the plasma. Suggested wavelengths for the determination of the elements in used oils are given in Table 1. For the analysis of sulfur, the spectrometer must be capable of operating in the wavelength region of 180 nm.

7.3 *Nebulizer*—A Babington-type^{8,9} high-solids nebulizer is strongly recommended. This type of nebulizer reduces the possibility of clogging and minimizes aerosol particle effects.

7.4 *Peristaltic Pump, (Recommended)*—A peristaltic pump is strongly recommended to provide a constant flow of solution. The pumping speed must be in the range 0.5 to 3 mL/min. The pump tubing must be able to withstand at least 6 h exposure to the dilution solvent. Viton tubing is typically used with hydrocarbon solvents, and poly-vinyl chloride tubing is typically used with methyl isobutyl ketone.

7.5 *Solvent Dispenser, (Optional)*—A solvent dispenser calibrated to deliver the required weight of dilution solvent for a ten-fold dilution of test specimen is very useful.

7.6 *Specimen Solution Containers*, of appropriate size, glass or plastic vials or bottles, with screw caps.

7.7 *Ultrasonic Homogenizer, (Recommended)*—A bath-type or probe-type ultrasonic homogenizer to homogenize the sample.

7.8 *Vortexer, (Optional)*—Vortexing the sample is an alternative to ultrasonic homogenization.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

such specifications are available.¹⁰ 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.

8.2 *Base Oil*—U.S.P. white oil, or a lubricating base oil that is free of analytes, and having a viscosity at room temperature as close as possible to that of the samples to be analyzed. (**Warning**—Lubricating base oils contain sulfur. For sulfur determinations, white oil is recommended for the preparation of standards.)

8.3 *Internal Standard*—Oil-soluble cadmium, cobalt, or yttrium (or any other suitable metal) are required when the internal standardization option is selected.

8.4 *Organometallic Standards*—Multi-element standards, containing 0.0500 mass % of each element, can be prepared from the individual concentrates. Refer to Practice D 4307 for a procedure for preparation of multicomponent liquid blends. When preparing multi-element standards, be certain that proper mixing is achieved. An ultrasonic bath is recommended. Standard multi-element concentrates, containing 0.0500 mass % of each element, are also satisfactory. (**Warning**—Some commercially available organometallic standards are prepared from metal sulfonates and therefore contain sulfur. For sulfur determinations, a separate sulfur standard would be required.)

NOTE 1—Secondary standards such as those prepared from petroleum additives, for example, can be used in place of those described. If the use of such secondary standards does not affect the analytical results by more than the repeatability of this test method.

8.5 *Sulfur Standard*—To use a metal sulfonate as a sulfur standard, analyze the sulfonate by Test Method D 1552. Alternatively, prepare a sulfur standard by diluting NIST SRM 1622c¹¹ in white oil.

8.6 *Dilution Solvent*—A solvent that is free of analytes and is capable of completely dissolving all standards and samples. Mixed xylenes, kerosine, and ortho-xylene were successfully used as dilution solvents in the interlaboratory study on precision.

9. Sampling

9.1 The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Thus, take lab samples in accordance with the instructions in Practice D 4057. The specific sampling technique can affect the accuracy of this test method.

10. Preparation of Apparatus

10.1 *Instrument*—Design differences between instruments, ICP excitation sources, and different selected analytical wavelengths for individual spectrometers make it impractical to detail the operating conditions. Consult the manufacturer's

⁸ Babington, R. S., *Popular Science*, May 1973, p. 102.

⁹ Fry, R. C. and Denton, M. B., *Analytical Chemistry*, Vol 49, 1977.

¹⁰ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

¹¹ Available from the National Institute of Standards and Technology, Gaithersburg, MD 20899.

instructions for operating the instrument with organic solvents. Set up the instrument for use with the particular dilution solvent chosen.

10.2 Peristaltic Pump—If a peristaltic pump is used, inspect the pump tubing and replace it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

10.3 ICP Excitation Source—Initiate the plasma source at least 30 min before performing analysis. During this warm up period, nebulize dilution solvent. Inspect the torch for carbon build-up during the warm up period. If carbon build-up occurs, replace the torch immediately and consult the manufacturer's operating guide to take proper steps to remedy the situation.

NOTE 2—Some manufacturers recommend even longer warm-up periods to minimize changes in the slopes of calibration curves.

10.4 Wavelength Profiling—Perform any wavelength profiling that may be called for in the normal operation of the instrument.

10.5 Operating Parameters—Assign the appropriate operating parameters to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (optional), interelement correction factors (optional), integration time, and internal standard correction (optional). Multiple integrations are required for each measurement, and the integration time is typically 10 s.

11. Calibration

11.1 The linear range must be established once for the particular instrument being used. This is accomplished by running intermediate standards between the blank and the working standard and by running standards containing higher concentrations than the working standard. Analyses of test specimen solutions must be performed within the linear range of response.

11.2 Working Standard—At the beginning of the analysis of each batch of specimens, perform a two-point calibration consisting of the blank and working standard. Use the check standard to determine if each element is in calibration. When the results obtained with the check standard are within 5 % of the expected concentrations for all elements, proceed with test specimen analyses. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration. Repeat this procedure with the check standard every five samples.

11.3 Working Standard with Internal Standard—Calibrate the instrument as described in 11.2. Obtain a printed record of the standard's emission intensities and those of the internal standard. Calculate an intensity ratio for each element by the following equation:

$$I(Re) = (I(e) - I(Be))/I(is) \quad (9)$$

where:

$I(Re)$ = intensity ratio for element e ,

$I(e)$ = intensity for element e ,

$I(Be)$ = intensity of the blank for element e , and

$I(is)$ = intensity of internal standard element.

11.3.1 Calculate the calibration factors from the intensity ratios. Alternatively, use the computer programs provided by

the instrument's manufacturer to calibrate the instrument using internal standardization.

12. Internal Standardization (Optional)

12.1 The internal standard procedure requires that every test specimen solution have the same concentration (or a known concentration) of an internal standard element that is not present in the original specimen. Specimen to specimen changes in the emission intensity of the internal standard element can be used to correct for variations in the test specimen introduction efficiency, which is dependent on the physical properties of the test specimen.

12.2 Internal Standard Solution—Weigh 20 g of 0.500 mass % cadmium, cobalt, or yttrium (or any other suitable metal) organometallic concentrate into a 1 L volumetric flask and dilute to 1 L with the dilution solvent. Prepare fresh, at least weekly, and transfer this solution into a dispensing vessel. The concentration of the internal standard element is not required to be 100 µg/mL; however, the concentration of the internal standard element in the test specimen solution should be at least 100 times its detection limit.

13. Sample Handling

13.1 Homogenization—It is extremely important to homogenize the used oil in the sample container in order to obtain a representative test specimen.

13.2 Ultrasonic Homogenization—Place the used oil (in the sample container) into the ultrasonic bath. For very viscous oils, first heat the sample to 60°C. Leave the sample in the bath until immediately before dilution.

13.3 Vortex Homogenization—As an alternative to ultrasonic homogenization, vortex mix the used oil in the sample container, if possible. For viscous oils, first heat the sample to 60°C.

14. Preparation of Test Specimens and Standards

14.1 Blank—Prepare a blank by diluting the base oil or white oil ten-fold by mass with the dilution solvent.

14.2 Working Standard, 10 µg/mL—Weigh 2 g of the 0.0500 mass % multi-element standard into a 4-oz. glass bottle, add 8 g of base oil and dilute with 90 g of dilution solvent. Working standards containing higher or lower concentrations can be prepared depending on the concentrations of additive elements, wear metals, or contaminants in the used oils. In addition, solutions containing single elements can also be prepared. However, ensure that the ten-fold dilution is maintained for all solutions.

14.3 Check Standards—Prepare instrument check standards in the same manner as the working standards such that the concentrations of elements in the check standards are similar to the concentrations of elements in the specimens.

14.4 Test Specimen—Weigh a portion of the well-homogenized sample into a suitable container. Add dilution solvent until the test specimen concentration is 10 mass %.

14.5 Internal Standard—If an internal standard is being used, add internal standard solution to the working standard, check standard, and test specimen before diluting with the dilution solvent. Ensure that the standard or test specimen

concentration is 10 mass %. Alternatively, the internal standard can be present in the dilution solvent.

15. Procedure and Calculation

15.1 *Analysis*—Analyze the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, etc.). Between test specimens, nebulize dilution solvent for 60 s. Calculate elemental concentrations by multiplying the determined concentration in the diluted test specimen solution by the dilution factor. Calculation of concentrations can be performed manually or by computer when such a feature is available.

15.2 *Quality Control with Check Standard*—Analyze the check standard after every fifth sample, and if any result is not within 5 % of the expected concentration, recalibrate the instrument and reanalyze the test specimens solutions back to the previous acceptable check standard analysis.

NOTE 3—To verify the accuracy and precision of the instrument calibration, certified standards such as SRM 1085 should be regularly analyzed.

15.3 *Analysis with Internal Standardization*—Analyze the test specimen solutions and calculate an intensity ratio for each of the elements found in the test specimen solutions using Eq 9 given in 11.3. From these intensity ratios, concentrations of the elements can be calculated.

16. Report

16.1 Report mg/kg to three significant figures for calcium, magnesium, zinc, barium, phosphorus, and sulfur. Report mg/kg to two significant figures for aluminum, boron, chromium, copper, iron, lead, manganese, molybdenum, nickel, potassium, sodium, silicon, silver, tin, titanium and vanadium.

17. Precision and Bias ¹²

17.1 *Precision*—The precision of this test method was determined by statistical analysis of interlaboratory results. In this study, dilution solvents were limited to xylene or kerosine. Some laboratories chose to use Babington-type nebulizers, peristaltic pumps, and background correction. Fourteen laboratories analyzed twelve specimens in duplicate. The samples were: one gas turbine used oil, four gasoline engine used oils, two truck diesel engine used oils, two marine engine used oils, SRM 1085¹¹ diluted in SRM 1083¹¹ (base oil) to contain approximately 40 mg/kg of eleven different metals (this oil also contained 8 mass % of an ethylene-propylene copolymer viscosity index improver), SRM 1085 diluted in SRM 1083 to contain approximately 40 mg/kg of twelve different metals, SRM 1085 diluted in SRM 1083 to contain approximately 2 mg/kg of 12 different metals.

¹² Interlaboratory study data are available from ASTM International Headquarters. Request RR:D02-1282.

17.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 and Table 4 only in one case in twenty.

17.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials, would in the long run, in the normal and correct operation of the test method, exceed the values in Table 3 and Table 5 only in one case in twenty.

17.1.3 Parametric representations of precision, calculated separately for the set of three base oil dilutions of NIST SRM 1085, are essentially the same, within experimental error, as the precision listed in Table 2 and Table 3.

17.2 *Bias*—Bias was evaluated by analyzing quantitative dilutions of SRM 1085, that contains oil-soluble metals rather than insoluble particulates. The means of the reported values for Al, Cr, Cu, Fe, Pb, Mg, Mo, Ni, Si, Ag, Sn, and Ti do not differ from the corresponding expected values by more than the repeatability of the method, when no significant interferences from other elements exist (see 6.1).

18. Keywords

18.1 additive-elements; aluminum; barium; boron; calcium; chromium; copper; emission-spectrometry; ICP; inductively coupled plasma atomic emission spectrometry; iron; lead; lubricating oils; magnesium; manganese; molybdenum; nickel; phosphorous, potassium; silicon; silver; sodium; sulfur; tin; titanium; vanadium; wear metals; zinc

TABLE 4 Calculated Repeatability (µg/g) at Selected Concentrations (mg/kg)

| Element | Concentration | | | |
|------------|---------------|-----|-----|------|
| | 1 | 10 | 100 | 1000 |
| Aluminum | ... | 1.8 | ... | ... |
| Barium | ... | ... | ... | ... |
| Boron | ... | 2.6 | ... | ... |
| Calcium | ... | ... | 1 | 32 |
| Chromium | 0.2 | 1.0 | ... | ... |
| Copper | ... | 1.0 | 8 | ... |
| Iron | ... | 0.8 | 5 | ... |
| Lead | ... | 3.3 | 7 | ... |
| Magnesium | ... | 1.2 | 8 | 61 |
| Manganese | ... | 0.2 | 4 | ... |
| Molybdenum | ... | 1.5 | 7 | ... |
| Nickel | ... | 1.6 | ... | ... |
| Phosphorus | ... | 4.9 | 19 | 71 |
| Potassium | ... | ... | 17 | 37 |
| Silicon | ... | 2.4 | ... | ... |
| Silver | 0.2 | 1.0 | ... | ... |
| Sodium | ... | 2.2 | ... | ... |
| Sulfur | ... | ... | ... | 130 |
| Tin | ... | 3.5 | ... | ... |
| Titanium | ... | 1.3 | ... | ... |
| Vanadium | 0.1 | 0.6 | ... | ... |
| Zinc | ... | ... | 8 | 65 |

TABLE 5 Calculated Reproducibility (µg/g) at Selected Concentrations (mg/kg)

| Element | Concentration | | | |
|------------|---------------|-----|-----|------|
| | 1 | 10 | 100 | 1000 |
| Aluminum | ... | 6.8 | ... | ... |
| Barium | 0.6 | ... | ... | ... |
| Boron | ... | 13 | ... | ... |
| Calcium | ... | ... | 6 | 120 |
| Chromium | 0.8 | 3.3 | ... | ... |
| Copper | ... | 2.4 | 24 | ... |
| Iron | ... | 3.3 | 21 | ... |
| Lead | ... | 6.9 | 16 | ... |
| Magnesium | ... | 4.2 | 25 | 150 |
| Manganese | ... | 2.1 | 33 | ... |
| Molybdenum | ... | 3.3 | 17 | ... |
| Nickel | ... | 4.7 | ... | ... |
| Phosphorus | ... | 14 | 43 | 140 |
| Potassium | ... | ... | 25 | 49 |
| Silicon | ... | 7.1 | ... | ... |
| Silver | 0.4 | 3.5 | ... | ... |
| Sodium | ... | 5.6 | ... | ... |
| Sulfur | ... | ... | ... | 210 |
| Tin | ... | 8.8 | ... | ... |
| Titanium | ... | 7.4 | ... | ... |
| Vanadium | 0.3 | 3.5 | ... | ... |
| Zinc | ... | ... | 13 | 170 |

SUMMARY OF CHANGES

Sub-Committee D02.03 has identified the location of selected changes to this standard since the last issue (D 5185 – 97) that may impact the use of this standard.

- (1) Updated the requirements for the *Specimen Solution Containers* in 7.6 to account for container sizes that fall out of the range previously specified, due to instrument or auto-sampler requirements.

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