



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

This standard is issued under the fixed designation D 5185; 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.

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

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 warning statements are given in 6.1, 8.2, and 8.4.

2. Referenced Documents

2.1 *ASTM Standards:*³

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

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

D 4057 ~~Practice for Manual Sampling of Petroleum and Petroleum Products~~

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 For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

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, 227.02, 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, 213.86, 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 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D 4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry
- D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy
- D 4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

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.

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	0.5–50 [†]	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, $\mu\text{g/g}$.

3.2.4 *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.

4. Summary of Test Method

4.1 A weighed portion of a thoroughly homogenized used oil is diluted tenfold 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.⁴ 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, *Kia*, 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, *Kia* is defined as:

$$Kia = Hi/Ha = Ii/(Ci \times Ha) \quad (3)$$

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 *Kia*. To apply these correction factors:

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

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

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

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

and, for more than one interferent:

$$Ca = Ca, \text{ apparent} - K1a \times C1 - K2a \times C2 - \dots \quad (8)$$

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

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 twenty-fold rather than tenfold 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., top loading or analytical, with automatic tare, capable of weighing to 0.001 g or 0.0001 g, with sufficient capacity to weigh prepared solutions.

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

⁴ 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.

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^{5,6} 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.⁷ 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 1622c⁸ 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 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/buildup during the warm up period. If carbon build-up/buildup occurs, replace the torch immediately and consult the manufacturer's operating guide to take proper steps to remedy the situation.

⁵ Babington, R. S., *Popular Science*, May 1973, p. 102.

⁶ Fry, R. C., and Denton, M. B., *Analytical Chemistry*, Vol 49, 1977.

⁷ *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 *Annual 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.

⁸ Available from the National Institute of Standards and Technology, Gaithersburg, MD 20899.

⁸ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

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. — Weigh a quantity of the 0.0500 mass % multi-element standard to the precision of the balance used (see 7.1) into an appropriately sized container, add four times the weight of the multi-element standard of base oil and dilute with 45 times the weight of the multi-element standard 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 tenfold dilution is maintained for all solutions.