



Designation: **D7303–17** **D7303 – 23**

Standard Test Method for Determination of Metals in Lubricating Greases by Inductively Coupled Plasma Atomic Emission Spectrometry¹

This standard is issued under the fixed designation D7303; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope*

1.1 This test method covers the determination of a number of metals such as aluminum, antimony, barium, calcium, iron, lithium, magnesium, molybdenum, phosphorus, silicon, sodium, sulfur, and zinc in unused lubricating greases by inductively coupled plasma atomic emission spectrometry (ICP-AES) technique.

1.1.1 The range of applicability for this test method, based on the interlaboratory study conducted in 2005,² is aluminum (10 to 600), antimony (10 to 2300), barium (50 to 800), calcium (20 to 50 000), iron (10 to 360), lithium (300 to 3200), magnesium (30 to 10 000), molybdenum (50 to 22 000), phosphorus (50 to 2000), silicon (10 to 15 000), sodium (30 to 1500), sulfur (1600 to 28 000), and zinc (300 to 2200), all in mg/kg. Lower levels of elements may be determined by using larger sample weights, and higher levels of elements may be determined by using smaller amounts of sample or by using a larger dilution factor after sample dissolution. However, the test precision in such cases has not been determined, and may be different than the ones given in [Table 3](#).

1.1.2 It may also be possible to determine additional metals such as bismuth, boron, cadmium, chromium, copper, lead, manganese, potassium, titanium, etc. by this technique. However, not enough data is available to specify the precision for these latter determinations. These metals may originate into greases through contamination or as additive elements.

1.1.3 During sample preparation, the grease samples are decomposed with a variety of acid mixture(s). It is beyond the scope of this test method to specify appropriate acid mixtures for all possible combination of metals present in the sample. But if the ash dissolution results in any visible insoluble material, the test method may not be applicable for the type of grease being analyzed, assuming the insoluble material contains some of the analytes of interest.

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

1.3 The development of the technique behind this test method is documented by Fox.³

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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

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² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1608. Contact ASTM Customer Service at service@astm.org.

³ Fox, B. S., "Elemental S., "Elemental Analysis of Lubricating Grease by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)," *J. ASTM International*, Vol 2, No. 8, 2005, pp. 12966.

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

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~~safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in Sections 8 and 10.

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:⁴

[D1193 Specification for Reagent Water](#)

[D3340 Test Method for Lithium and Sodium in Lubricating Greases by Flame Photometer](#) (Withdrawn 2013)⁵

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

[D4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry](#)

[D5185 Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry \(ICP-AES\)](#)

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

[D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories](#)

[D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry \(ICP-AES\) for Elemental Analysis of Petroleum Products and Lubricants](#)

3. Terminology

3.1 *Definitions*—Refer to terminology identified in Test Method [D5185](#) for spectroscopy terms used in this standard.

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology [D4175](#).

3.1.2 Refer to terminology identified in Test Method [D5185](#) for spectroscopy terms used in this standard.

4. Summary of Test Method

4.1 A weighed portion of the grease sample is weighed and subjected to alternate means of sample dissolution which may include sulfated ashing in a muffle furnace or by closed vessel microwave digestion in acid. Ultimately these diluted acid solutions are analyzed using ICP-AES. Aqueous calibration standards are used. 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 those measured with the calibration standards, the concentrations of elements in the test specimen can be calculated.

4.2 Additional information on using inductively coupled plasma-atomic emission spectrometry can be found in Practice [D7260](#).

5. Significance and Use

5.1 Lubricating greases are used in almost all bearings used in any machinery. Lubricating grease is composed of ~90 % additized oil and soap or other thickening agent. There are over a dozen metallic elements present in greases, either blended as additives for performance enhancements or as thickeners, or in used greases present as contaminants and wear metals. Determining their concentrations can be an important aspect of grease manufacture. The metal content can also indicate the amount of thickeners in the grease. Additionally, a reliable analysis technique can also assist in the process of trouble shooting problems with new and used grease in the field.

5.2 Although widely used in other sectors of the oil industry for metal analysis, ICP-AES based Test Methods [D4951](#) or [D5185](#)

⁴ 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.

⁵ The last approved version of this historical standard is referenced on www.astm.org.

cannot be used for analyzing greases because of their insolubility in organic solvents used in these test methods. Hence, grease samples need to be brought into aqueous solution by acid decomposition before ICP-AES measurements.

5.3 Test Method **D3340** has been used to determine lithium and sodium content of lubricating greases using flame photometry. This technique is no longer widely used. This new test method provides a test method for multi-element analysis of grease samples. This is the first D02 standard available for simultaneous multi-element analysis of lubricating greases.

6. Interferences

6.1 *Spectral*—Spectral interferences can usually be avoided by judicious choice of analytical wavelengths. There are no known spectral interferences between elements covered by this test method when using the spectral lines listed in **Table 21**. However, if spectral interferences exist because of other interfering elements or selection of other spectral lines, correct for the interferences using the technique described in Test Method **D5185**.

6.1.1 Follow the instrument manufacturer’s operating guide to develop and apply correction factors to compensate for the interferences.

6.2 *Chemical*—If the grease sample contains refractory additives such as silicon or molybdenum, it is possible that some of these elements may remain undissolved in the residue, and may result in lower recoveries.

6.2.1 If HF is used for dissolution of grease residues, elements such as silicon may be lost as SiF₆. Residual HF can also attack the ICP sample introduction system. HF can be passivated by adding dilute boric acid to the acid solution.

6.2.2 If the dry ashing in sample preparation step is used, elements such as sulfur will be volatilized during combustion.

7. Apparatus

7.1 *Analytical Balance*, capable of weighing to 0.001 g or 0.0001 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 elements in dissolved grease solutions are given in **Table 21**.

7.3 *Peristaltic Pump, (Recommended)*—A peristaltic pump is strongly recommended to provide a constant flow of solution. The pumping speed must be in the range of 0.5 mL/min to 3 mL/min. The pump tubing must be able to withstand at least 6 h exposure to solutions.

7.4 *Specimen Solution Containers*, of appropriate size, glass or polyolefin vials or bottles, with screw caps without metal liners.

TABLE 21 Suggested Wavelengths^{A,B} for Elements Determined in Grease Samples

Element	Wavelength, nm
Aluminum	167.038, 308.22, 396.15, 309.27
Antimony	206.83, 217.58, 231.15
Barium	223.53, 233.527, 455.40, 493.41
Calcium	315.88, 317.93, 364.4, 396.85, 422.67
Iron	238.20, 259.94
Lithium	670.78, 610.36, 460.29
Magnesium	279.08, 279.55, 280.278, 285.21
Molybdenum	135.387, 202.03, 281.62
Phosphorus	177.51, 178.29, 213.62, 214.91, 253.40
Silicon	288.16, 251.618
Sodium	589.595
Sulfur	182.04, 180.73, 182.63
Zinc	202.55, 206.20, 213.86, 334.58, 481.05

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

^B Wavelengths for boron, phosphorus, and sulfur below 190 nm require that a vacuum or inert gas purge optical path be used.

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.⁶ 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 *Sulfuric Acid*, concentrated sulfuric acid, H₂SO₄. (**Warning**—Causes severe burns. Corrosive.)

8.3 *Nitric Acid*, concentrated nitric acid, HNO₃. (**Warning**—Causes severe burns. Corrosive.)

8.4 *Hydrochloric Acid*, concentrated hydrochloric acid, HCl. (**Warning**—Causes burns.)

8.5 *Hydrofluoric Acid*, concentrated hydrofluoric acid, HF (**Warning**—Causes severe burns.)

8.6 *Aqueous Standard Solutions*, individual aqueous elemental standards with 100 mg/L concentrations of elements of interest. These can be prepared by dissolving pure metal compounds in water or dilute acids, or may be purchased from commercial sources.

8.6.1 Multi-element aqueous standards may be advantageous to use.

8.6.2 *Internal Standard*, aqueous cobalt, indium, scandium, yttrium or other single element standard, not a component of the grease test specimen or calibration standard, nominal 500 mg/kg concentration.

8.7 *Water*, distilled or deionized water, unless otherwise indicated, references to water shall be understood to mean Type II reagent grade water as defined in Specification **D1193**.

8.8 *Quality Control (QC) Samples*, preferably are portions of one or more grease materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section **15**.

8.9 *Microwave Oven*, commercially available laboratory microwave digestion oven of sufficient power (for example, at least 1000 W) is suitable. The microwave digestion dishes are also commercially available. (**Warning**—Take all necessary precautions to prevent exposure to radiofrequency radiation.)

8.10 *Microwave Sample Digestion System*, with closed-vessel silicon-free polytetrafluoroethylene (PTFE) digestion vessels. The vessels need to be capable of withstanding the pressure generated from the digestion of 0.2 g of sample (pressure achieved with a 100 mL vessel and 0.2 g of sample could be in excess of 100 psi). Microwave digestions systems with temperature and pressure monitoring are recommended for safety and accuracy of sample preparation.

8.11 The test method requires essentially microwave transparent and reagent resistant suitably inert polymeric materials (examples are PFA or TFM) to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The vessels internal volume should be at least 45 mL, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief. These specifications are given to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

8.12 *Rotating Turntable*, to insure homogeneous distribution of microwave radiation within most systems. The speed of the turntable should be a minimum of 3 r/min.

⁶ *Reagent Chemicals, American Chemical Society Specifications, 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.

8.13 *Combustion Dishes*, Vycor or platinum evaporation dishes of 250 mL size.

8.14 *Volumetric Flasks*, polypropylene or similar material of 25 mL and 50 mL sizes.

8.15 *Electric Muffle Furnace*, capable of maintaining $525\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ and sufficiently large to accommodate several 250 mL beakers. The capacity of an oxygen bleed is advantageous and optional. (**Warning**—Take all necessary precautions to prevent exposure to very hot surfaces.)

8.16 *Heating Lamp*, commercial infrared heating lamp.

9. Sampling

9.1 The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Thus, take laboratory samples in accordance with the instructions in Practice D4057. The specific sampling technique can affect the accuracy of this test method.

10. Preparation of Samples

10.1 Sulfated Ash Digestion:

10.1.1 Accurately weigh approximately 1 g to $2\text{ g} \pm 0.1\text{ g}$ of the grease sample in a Vycor or platinum container of suitable size. Char the sample on a hot plate until it is reduced to $\sim 0.5\text{ g}$. A heat lamp may be used to assist in this process.

10.1.2 After the charred residue is cooled, add 1 mL to 2 mL of concentrated sulfuric acid and carefully heat on the hot plate taking care to avoid spattering of the contents, and continue heating until the fumes are no longer evolved.

10.1.3 Place the charred sample in a muffle furnace at $525\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ until the oxidation of the carbon is practically complete. This typically takes about 2 h.

10.1.4 If the ashing is not complete as indicated by presence of black color of the residue, repeat step 10.1.2 to complete the sulfation.

10.1.5 Add about 5 mL of concentrated nitric, hydrochloric or other appropriate mineral acid to the residue, and heat gently to dissolve the remaining solids.

10.1.6 Dilute the solution to volume with deionized water in a 25 mL or a 50 mL volumetric flask.

NOTE 1—The dilutions may be carried out on a weight or volume basis.

10.2 Closed Vessel Microwave Oven Digestion:

10.2.1 Accurately weigh about 0.1 g to 1 g of the grease sample in a polytetrafluoroethylene (PTFE) digestion vessel with pressure relief mechanism. Add about 4 mL of concentrated nitric, hydrochloric, or other appropriate mineral acid.

NOTE 2—From a safety view point when digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 1 g can be used.

NOTE 3—Some microwave oven models may be capable of simultaneously processing multiple sample digestion vessels.

10.2.2 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the test method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within $\pm 2.5\text{ }^{\circ}\text{C}$ and permit adjustment of the microwave output power within 2 s.

10.2.3 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching

between high concentration and low concentration samples, all digestion vessels (fluoropolymer liners only) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80 °C, but less than boiling) for a minimum of 2 h followed with hot (1:1) nitric acid (greater than 80 °C, but less than boiling) for a minimum of 2 h and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10 % V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.

10.2.3.1 Alternate cleaning procedures may be utilized if they are shown to be satisfactory.

10.2.4 The analyst should be aware of the potential for a vigorous reaction. If a vigorous reaction occurs upon the initial addition of reagent or the sample is suspected of containing easily oxidizable materials, allow the sample to predigest in the uncapped digestion vessel. Heat may be added in this step for safety considerations (for example, the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

10.2.5 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to the manufacturer's specifications.

10.2.6 Pressure control for a specific matrix is applicable if instrument conditions are established using temperature control. Because each matrix will have a different reaction profile, performance using temperature control must be developed for every specific matrix type prior to use of the pressure control system. At the end of the microwave program, allow the vessels to cool for a minimum of 5 min before removing them from the microwave system.

10.2.7 Program the microwave oven to heat at 125 W for 15 min, then ramp up to 190 W for another 15 min.

NOTE 4—Different microwave oven models may require different temperature ramping and holding profiles.

NOTE 5—Care must be taken to keep internal temperature and pressure within the capability of the vessels used. Excessive heat and pressure will cause the digestion pressure vessels to deform and potentially leak.

10.2.8 Detailed safety recommendations specific to the model and manufacturer of the microwave digestion system is beyond the scope of this test method. The user of this test method is advised to consult the equipment manual, the manufacturer and other literature sources for proper safe operation of the digestion system. The user should be advised that digestion of samples within the scope of this test method could rapidly generate high pressure beyond the mechanical capacity of the vessel, which may cause a rupture of the vessel and damage to the digestion system. (**Warning**—Exercise caution when handling vessels after they have been heated since they may possess high internal pressures.)

10.2.8.1 **Warning**—The outer layers of vessels are frequently not as acid or reagent resistant as the liner material and must not be chemically degraded or physically damaged to retain the performance and safety required. Routine examination of the vessel materials may be required to ensure their safe use.

10.2.8.2 **Warning**—Another safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. However, many digestion vessels constructed from certain suitably inert polymeric materials may crack, burst, or explode in the unit under certain pressures. Only suitably inert polymeric (such as PFA or TFM and others) containers with pressure relief mechanisms or containers with suitably inert polymeric liners and pressure relief mechanisms are considered acceptable. Users are therefore advised not to use domestic (kitchen) type microwave ovens or to use inappropriate sealed containers without pressure relief for microwave acid digestions by this test method. Use of laboratory-grade microwave equipment is required to prevent safety hazards.

10.2.8.3 **Warning**—Laboratories should not use domestic (kitchen) type microwave ovens for this test method. There are several significant safety issues. First, when an acid such as nitric is used to effect sample digestion in microwave units in sealed vessels equipment, there is the potential for the acid gas vapor released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.

10.2.8.4 **Warning**—Toxic nitrogen oxide(s), hydrogen fluoride, and toxic chlorine (from the addition of hydrochloric acid) fumes

are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.

10.2.8.5 Warning—The analyst should wear protective gloves and face protection and must not at any time permit a solution containing acid to come in contact with skin or lungs.

10.2.9 After the heating cycle is complete, place the heating pressure vessels in an ice bath for at least an hour to cool. Quantitatively transfer the dissolved sample into a 25 mL volumetric flask and bring it up to volume with deionized water. (Also, see **Note 1.**)

NOTE 6—Care must be exercised when opening the pressure vessel so that the contents do not spill out.

NOTE 7—There may be some insoluble residue at the end of dissolution steps above if the grease sample contains refractory elements such as silicon, molybdenum, barium, etc. In such cases use of hydrofluoric acid to dissolve the residue may be required. If HF is used, HF-resistant labware must be used during the dissolution steps. Also, an HF-resistant ICP sample introduction system should be used if silicon is to be quantified and to minimize potential damage to the “solution wetted” glass components in the ICP. Some post-digestion organic residue may also remain in the microwave digestion vessels and seals. They can be identified as floating immiscible organic residue or “ring” around the liquid level of the microwave digestion vessel, most likely leached of any analyte and not containing any metals.

11. Preparation of ICPAES Instrument

11.1 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.

11.2 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.

11.3 ICP Excitation Source—Initiate the plasma source at least 30 min before performing an analysis. During this warm up period, nebulize either water or a dilute (5 %) acid solution.

NOTE 8—Some instrument manufacturers recommend even longer warm-up periods to minimize changes in the slopes of calibration curves.

11.4 Wavelength Profiling—Perform any wavelength profiling that is specified in the normal operation of the instrument.

11.5 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(s), background correction points (optional), interelement correction factors (see **6.1**), and integration time. Multiple integrations (typically three) are required for each measurement. A typical measurement time is 10 s.

NOTE 9—Typical ICP operating conditions follow. Different conditions specific to different instruments may be used.

Forward Power	1100 W to 1500 W
Coolant Gas, Argon	12 L/min to 17 L/min
Auxiliary Gas, Argon	0.2 L/min to 1 L/min
Nebulizer Gas, Argon	0.7 L/min to 1.1 L/min
Sample Uptake Rate	1 mL/min to 2 mL/min

12. Preparation of Calibration Standards

12.1 Blank—Prepare a blank solution by adding same concentration of diluted acids as used in the sample dissolution (usually 5 % nitric acid).

12.2 Working Standards—Prepare by diluting stock standard solutions (see **8.6**) to appropriate levels, usually 1 mg/L to 10 mg/L concentration with dilute nitric acid solution.

12.3 Check Standards—Prepare instrument check standards in the same manner as working standards such that the concentration of the elements in the check standards are similar to the concentration of elements in the test specimen solutions.