



Standard Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc In Unused Lubricating Oils By Atomic Absorption Spectrometry¹

This standard is issued under the fixed designation D 4628; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

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

1. Scope

1.1 This test method is applicable for the determination of mass percent barium from 0.005 to 1.0 %, calcium and magnesium from 0.002 to 0.3 %, and zinc from 0.002 to 0.2 % in lubricating oils.

1.2 Higher concentrations can be determined by appropriate dilution. Lower concentrations of metals such as barium, calcium, magnesium, and zinc at about 10 ppm level can also be determined by this test method. Use of this test method for the determination at these lower concentrations should be by agreement between the buyer and the seller.

1.3 Lubricating oils that contain viscosity index improvers may give low results when calibrations are performed using standards that do not contain viscosity index improvers.

1.4 The values stated in SI units are to be regarded as the 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 practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Note 1, Note 5, and Note 7.

2. Summary of Test Method

2.1 A sample is weighed and base oil is added to 0.25 ± 0.01 -g total mass. Fifty millilitres of a kerosine solution, containing potassium as an ionization suppressant, are added, and the sample and oil are dissolved. (**Warning**—See Note 2.) Standards are similarly prepared, always adding oil if necessary to yield a total mass of 0.25 g. These solutions are burned in the flame of an atomic absorption spectrophotometer. An acetylene/nitrous oxide flame is used. (**Warning**—See Note 1.)

NOTE 1—**Warning:** Combustible. Vapor harmful.

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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NOTE 2—**Warning:** Hazardous. Potentially toxic and explosive.

3. Significance and Use

3.1 Some oils are formulated with metal-containing additives that act as detergents, antioxidants, antiwear agents, etc. Some of these additives contain one or more of these metals: barium, calcium, zinc, and magnesium. This test method provides a means of determining the concentration of these metals that gives an indication of the additive content in these oils.

4. Apparatus

4.1 *Atomic Absorption Spectrophotometer.*

4.2 *Analytical Balance.*

4.3 *Automatic Measuring Pipet or Volumetric Class A Pipet, 50-mL capacity.*

4.4 *Bottles with Screw Caps, 60 mL (2 oz).*

NOTE 3—Suitable volumetric flasks or plastic bottles may be substituted.

4.5 *Shaker, Mechanical Stirrer, or Ultrasonic Bath, capable of handling 60-mL bottles.*

5. Reagents

5.1 *Base Oil*, metal-free, with a viscosity of about 4 cSt at 100°C. A100 neutral oil which provides good solvency for standards and additive concentrate is satisfactory. Highly paraffinic oils should be avoided.

5.2 *2-Ethyl Hexanoic Acid*, which has been determined to be free of interfering metals.

5.3 *Kerosine, Metal-Free* (Note 4)—(See Note 5, Note 6, and **Warning** Note 7), distillation range from 170°C to 280°C at 100 kPa (1 atm). When the kerosine solvent is contaminated, it may be purified metal-free by running through attapulugus clay.

NOTE 4—Solvents other than kerosene, such as xylene MEK and so forth, may be used in this test method, however, the precision data quoted in Section 16 was obtained using kerosene.

NOTE 5—Metal-free kerosine can be obtained from most laboratory supply houses, but should be tested for metal content before using.

NOTE 6—Satisfactory results have been obtained in this test method by using Baker “kerosine” (deodorized) which has typical initial and end boiling points of 191°C and 240°C, respectively, and a typical composition of 96.7 volume % saturates, 0.1 volume % olefins, and a maximum of 3.2 volume % aromatics. If the kerosine used by an operator deviates appreciably from this composition, there may be significant error.

NOTE 7—**Warning:** Combustible. Vapor harmful.

5.4 *Oil-Soluble Metal Compounds*,² stock standard blend in base oil. A 0.25 ± 0.01-g portion of this stock standard blend diluted with 50 mL of the potassium ionization suppressant solution (see 5.5) shall yield a reading of 0.5 ± 0.1 absorbance units for each of the elements barium, calcium, magnesium, and zinc using a minimum of scale expansion or burner rotation. The concentrations of the metal should be blended accurately to three significant figures. The actual concentrations should be chosen to conform to the optimum working range of the particular instrument being used, but as a guide one cooperator used 0.4 % barium, 0.03 % calcium, 0.03 % magnesium, and 0.06 % zinc. The stock standard blend should be heated and stirred to ensure a homogeneous solution.

NOTE 8—In addition to the calibration standards identified in 5.4, 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), and analytical techniques to establish the elemental concentration mass percent levels.

² Oil soluble metal compounds found satisfactory for this method are available from National Institute of Standards and Technology, Office of Standard Reference Materials, Washington, DC 20234.

5.5 *Potassium Ionization Suppressant Solution*—containing an oil-soluble potassium compound in kerosine at 2.0 ± 0.1 g potassium/litre of solution.

NOTE 9—The actual potassium concentration needed varies with the source of potassium and perhaps the instrumental conditions as well. To determine the needed concentration, atomize solutions containing 0, 500, 1000, 1500, 2000, 2500, and 3000 ppm potassium with 25 ppm barium and 5 ppm calcium in each. Plot graphs of barium and calcium absorbance versus potassium concentration as shown in Fig. 1. The minimum concentration of potassium needed is that above the knee for both the barium and calcium curves.

5.6 *Working Standards*—Freshly prepared by weighing into six 60-mL bottles (1) 0.25, (2) 0.20, (3) 0.15, (4) 0.10, (5) 0.05, and (6) 0 g of stock standard blend (see 5.4) to three significant figures and add 0.0, 0.05, 0.10, 0.15, 0.20, and 0.25 ± 0.01 g of base oil, respectively. Add 50 mL of potassium ionization suppressant solution (see 5.5) to each bottle and shake or stir to dissolve.

NOTE 10—Many modern AAS instruments can store up to 3 or 4 calibration standards in memory. In such cases, follow the manufacturer’s instructions, ensuring that the unknown sample’s absorbance is in the linear part of the calibration range used.

6. Sampling

6.1 Shake the sample thoroughly before sampling to ensure obtaining a representative sample.

7. Preparation of Apparatus

7.1 Consult the manufacturer’s instructions for the operation of the atomic absorption spectrophotometer. The present test method assumes that good operating procedures are

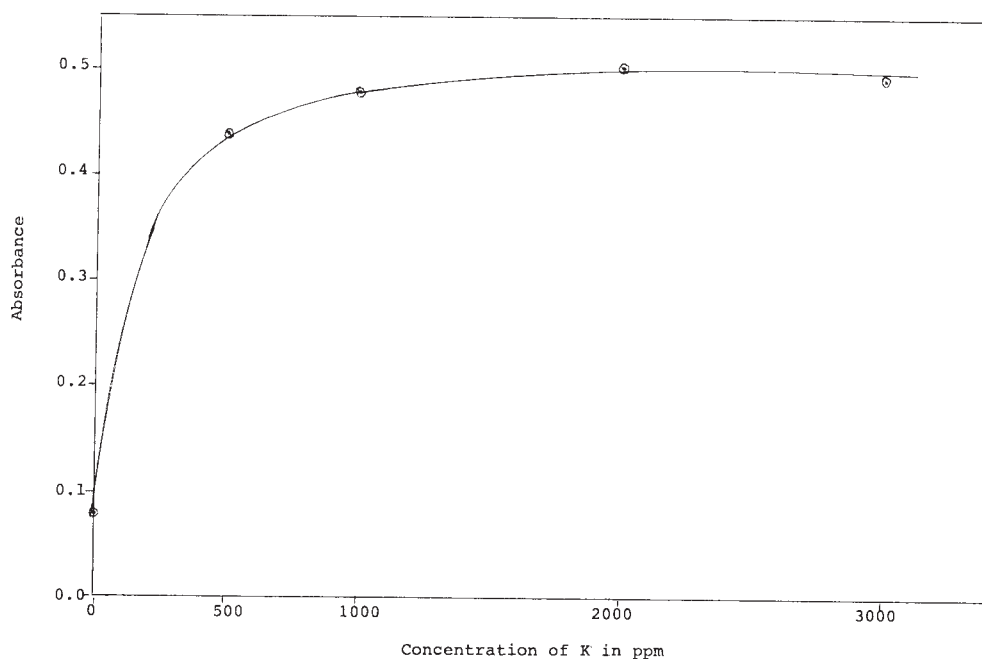


FIG. 1 Plot Graphs for Barium and Calcium