



Designation: D4628 – 23

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 D4628; 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 U.S. 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 standard. No other units of measurement are included in 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in 4.1, 7.3, and 9.1.

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.*

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. Referenced Documents

2.1 *ASTM Standards*:²

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

4. Summary of Test Method

4.1 A sample is weighed and base oil is added to 0.25 g \pm 0.01 g total mass. Fifty millilitres of a kerosene solution, containing potassium as an ionization suppressant, are added, and the sample and oil are dissolved. (**Warning—Hazardous.** Potentially toxic and explosive.) 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—Combustible.** Vapor harmful.)

5. Significance and Use

5.1 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.

5.2 Several additive metals and their compounds are added to the lubricating oils to give beneficial performance. (See Table 1.)

² 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 Lubricants and Additive Materials

| Element | Compounds | Purpose/Application |
|-----------|--|---|
| Barium | Sulfonates, phenates | Detergent inhibitors, corrosion inhibitors, detergents, rust inhibitors, automatic transmission fluids |
| Calcium | Sulfonates, phenates | Detergent inhibitors, dispersants |
| Magnesium | Sulfonates, phenates | Detergent inhibitors |
| Zinc | Dialkyldithiophosphates, dithiocarbamates, phenolates carboxylates | Anti-oxidant, corrosion inhibitors, antiwear additives, detergents, crankcase oils, hypoid gear lubricants, aircraft piston engine oils, turbine oils, automatic transmission fluids, railroad diesel engine oils, brake lubricants |

6. Apparatus

6.1 *Atomic Absorption Spectrophotometer.*

6.2 *Analytical Balance.*

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

6.4 *Bottles with Screw Caps, 60 mL.*

NOTE 1—Suitable volumetric flasks or plastic bottles may be substituted.

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

7. Reagents

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

7.2 *2-Ethyl Hexanoic Acid*, which has been determined to be free of interfering metals.

7.3 *Kerosene, Metal-Free*—See **Notes 2-4. (Warning—Combustible. Vapor harmful.)** Distillation range from 170 °C to 280 °C at 100 kPa (1 atm). When the kerosene solvent is contaminated, it may be purified metal-free by running through attapulugus clay.

NOTE 2—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 17 was obtained using kerosene.

NOTE 3—Metal-free kerosene can be obtained from most laboratory supply houses, but should be tested for metal content before using.

NOTE 4—Satisfactory results have been obtained in this test method by using Baker “kerosene” (deodorized) which has typical initial and end boiling points of 191 °C and 240 °C, respectively, and a typical composition of 96.7 % by volume saturates, 0.1 % by volume olefins, and a maximum of 3.2 % by volume aromatics. If the kerosene used by an operator deviates appreciably from this composition, there may be significant error.

7.4 *Oil-Soluble Metal Compounds*, stock standard blend in base oil. A 0.25 g ± 0.01 g portion of this stock standard blend diluted with 50 mL of the potassium ionization suppressant solution (see 7.5) 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 5—In addition to the calibration standards identified in 7.4, 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.

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

NOTE 6—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 ppm, 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm, 2500 ppm, 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.

7.6 *Working Standards*—Freshly prepared by weighing into six 60 mL bottles (1) 0.25 g, (2) 0.20 g, (3) 0.15 g, (4) 0.10 g, (5) 0.05 g, and (6) 0 g of stock standard blend (see 7.4) to three significant figures and add 0.0 g, 0.05 g, 0.10 g, 0.15 g, 0.20 g, and 0.25 g ± 0.01 g of base oil, respectively. Add 50 mL of potassium ionization suppressant solution (see 7.5) to each bottle and shake or stir to dissolve.

NOTE 7—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.

7.7 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum 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 17.

8. Sampling

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

9. Preparation of Apparatus

9.1 Consult the manufacturer’s instructions for the operation of the atomic absorption spectrophotometer. The present test method assumes that good operating procedures are followed. Design differences between spectrophotometers

Barium
K Ionization Suppressant in Kerosine Solvent

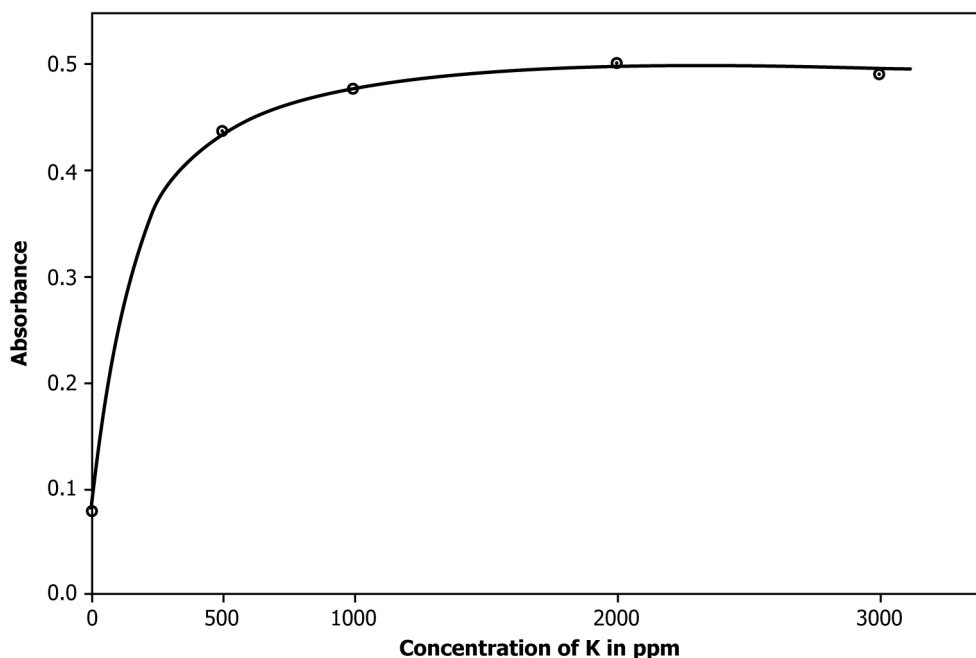


FIG. 1 Plot Graphs for Barium and Calcium

make it impractical to specify the required manipulations in detail here. (**Warning**—Proper operating procedures are required for safety as well as for reliability of results. An explosion can result from flame blow-back unless the correct burner head and operating sequence are used.)

9.2 For the barium determination, fit the barium hollow cathode lamp and set the monochromator at 553.6 nm. Make fine adjustments to the wavelength setting to give maximum output. Using the correct burner head for acetylene/nitrous oxide, set up the acetylene/nitrous oxide flame. On instruments where applicable, adjust the gain control to set this maximum at full scale, when aspirating standard (6) in 7.6.

9.3 Aspirate at about 2.5 mL/min to 3 mL/min a standard barium solution into the flame. Make adjustments to the height and angle of the burner and to the acetylene flow rate to give maximum absorption. Make sure that standard (6) in 7.6 still gives zero absorbance by making adjustments, if necessary.

10. Calibration (Barium)

10.1 Aspirate standard (1) in 7.6. With a minimum of scale expansion or burner rotation, obtain a reading of 0.5 ± 0.1 on the absorbance meter or alternative readout device.

10.2 Aspirate the standards of 7.6 sequentially into the flame and record the output (or note the meter deflections). Aspirate the solvent alone after each standard.

10.3 Determine the net absorbance of each standard. If the spectrophotometer output is linear in absorbance, the net absorbance is given by the difference between the absorbance for the standard or sample solution and the absorbance for the solvent alone. If the spectrophotometer output is proportional to transmission (that is, to light intensity) then the net absor-

bance is given by $\log_{10} d_0/d_1$, where the deflections are d_0 when solvent alone is aspirated and d_1 when the standard or sample solution is aspirated.

10.4 Plot the net absorbance against the concentration (mg/50 mL suppressant solution) of barium in the standards to give a calibration curve.

NOTE 8—The calibration curve may be automatically calculated by the instrument software and displayed by way of the instrument computer terminal, making actual plotting unnecessary.

10.5 Calibration must be carried out prior to each group of samples to be analyzed and after any change in instrumental conditions, as variation occurs in the instrument behavior. Readings may also vary over short times from such causes as buildup of deposits on the burner slot or in the nebulizer. Thus, a single standard should be aspirated from time to time during a series of samples to check whether the calibration has changed (a check after every fifth sample is recommended). The visual appearance of the flame also serves as a useful check to detect changes of condition.

10.6 Determine the slope and intercept for barium based on the calibration curve developed. The values will be used to determine barium concentrations of samples to be tested. Ensure that the regression coefficient is at least 0.99 for barium, otherwise the laboratory needs to re-calibrate for barium when this criteria is not satisfied.

11. Procedure (Barium)

11.1 Weigh the sample to three significant figures into a 60 mL bottle. The sample mass is chosen to give an absorbance reading of 0.2 to 0.5. Add base oil to make $0.25 \text{ g} \pm 0.01 \text{ g}$ total mass. Add 50 mL of potassium suppressant solution, see

7.5, and dissolve. The maximum sample size to be used is 0.25 g, and the minimum is 0.05 g.

11.1.1 To hazy samples add 0.25 mL ± 0.01 mL of 2-ethyl hexanoic acid and shake. If this clears up the haze, the analysis is run, and the dilution error is corrected by multiplying the found results by 1.005. If the sample remains hazy, the sample is not suitable to be analyzed by this test method.

11.2 Samples yielding absorbances greater than 0.5 even with the minimum sample size can be accurately diluted with new base oil to a suitable concentration. Make sure the new solution is homogeneous before proceeding as instructed in 11.1.

11.3 Aspirate the sample solution and determine the absorbance, aspirating solvent alone before and after each reading.

12. Calculation (Barium)

12.1 Read from the calibration curve the concentration, *C*, corresponding to the measured absorbance.

C = concentration of barium in the diluted sample solution, mg/50 mL of suppressant solution.

12.2 Calculate the barium content of the oils in percent mass as follows:

$$\text{Barium, \% mass} = \frac{CD}{10W} \quad (1)$$

where:

W = grams of sample/50 mL,

C = milligrams of metal/50 mL, and

D = dilution factor if dilution was necessary in 11.2.

NOTE 9—If the calibration curve is linear, the concentration may be determined by an equation instead of a calibration curve.

13. Calcium Determination

13.1 Repeat Sections 8 through 11 replacing references made to barium with calcium using the following conditions:

13.1.1 Acetylene/nitrous oxide flame,

13.1.2 Calcium hollow cathode lamp, and

13.1.3 Analytical line 422.7 nm.

14. Magnesium Determination

14.1 Repeat Sections 8 through 11 replacing references made to barium with magnesium using the following conditions:

14.1.1 Acetylene/nitrous oxide flame,

14.1.2 Magnesium hollow cathode lamp, and

14.1.3 Analytical line 285.2 nm.

15. Zinc Determination

15.1 Repeat Sections 8 through 11 replacing references made to barium with zinc using the following conditions:

15.1.1 Acetylene/nitrous oxide flame,

15.1.2 Zinc hollow cathode lamp, and

15.1.3 Analytical line 213.9 nm.

NOTE 10—Although this test method has been described for the determination of four elements on a single sample, the sequence of operations in analyzing several samples should also be considered. Aspiration of a sample to determine its absorbance is very quick.

TABLE 2 Repeatability

| Element | Range, Mass % | Repeatability |
|-----------|---------------|---------------|
| Barium | 0.005–1.0 | 0.0478x % |
| Calcium | 0.002–0.3 | 0.0227x % |
| Magnesium | 0.002–0.3 | 0.0168x % |
| Zinc | 0.002–0.2 | 0.0247x % |
| Calcium | 1.7 | 0.032 |
| Zinc | 1.0 | 0.025 |

Changing wavelength setting and lamps takes longer. Thus, it is most economical to make measurements at a single wavelength on a series of samples and standards before changing conditions.

16. Report

16.1 Report concentrations greater than 0.1 % to three significant figures.

16.2 Concentrations between 0.005 % to 0.1 % barium and 0.002 % to 0.1 % zinc, calcium, and magnesium are reported to two significant figures.

16.3 Concentrations less than the lower limits in 16.2 shall be reported as less than the appropriate lower limit.

17. Quality Control

17.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (see 7.7).

17.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

17.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

18. Precision and Bias³

18.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

18.1.1 *Repeatability*—The difference between the 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 this test method, exceed the values in Table 2 only in one case in twenty.

18.1.2 *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 this test method, exceed the values in Table 3 only in one case in twenty.

NOTE 11—The values of these precision estimates for selected values of *x* are set out in Table 4.

NOTE 12—The precision data in Section 18 was obtained by using samples containing higher concentration levels of metals and may not be representative of the precision at about 10 ppm concentration levels.

18.2 Bias:

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1207. Contact ASTM Customer Service at service@astm.org.