Standard Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry[1]

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 3.1, 6.3, and 8.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance[2]

3. Summary of Test Method

3.1 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—**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.)

4. Significance and Use

4.1 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. Apparatus

5.1 *Atomic Absorption Spectrophotometer*.

5.2 *Analytical Balance*.

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

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

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

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

6. Reagents

6.1 *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.

6.2 *2-Ethyl Hexanoic Acid*, which has been determined to be free of interfering metals.

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[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] *Annual Book of ASTM Standards*, Vol 05.03.

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

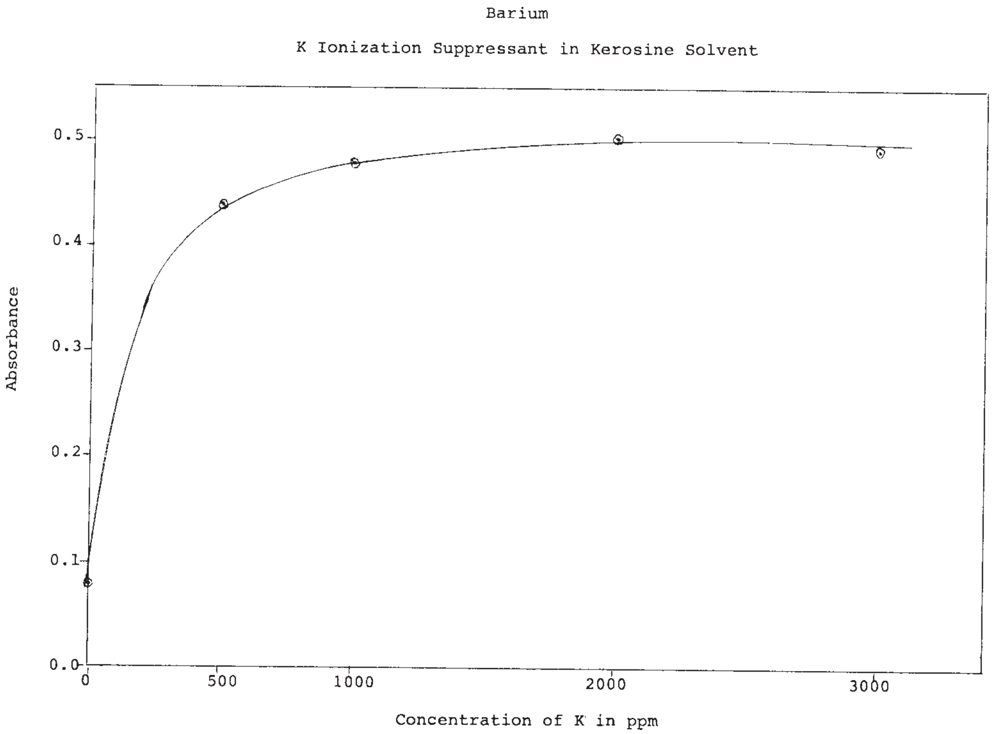

FIG. 1 Plot Graphs for Barium and Calcium

6.3 *Kerosine, 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 kerosine solvent is contaminated, it may be purified metal-free by running through attapulgus clay.

NOTE 2—Solvents other than kerosine, 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 kerosine.

NOTE 3—Metal-free kerosine 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 "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.

6.4 *Oil-Soluble Metal Compounds*,[3] 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 6.5) 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 6.4, 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.

6.5 *Potassium Ionization Suppressant Solution*—containing an oil-soluble potassium compound in kerosine at 2.0 ± 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, 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.

6.6 *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 6.4) 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 6.5) 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.

6.7 *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

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

can be used to check the validity of the testing process as described in Section 16.

7. Sampling

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

8. Preparation of Apparatus

8.1 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 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.)

8.2 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 6.6.

8.3 Aspirate at about 2.5 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 6.6 still gives zero absorbance by making adjustments, if necessary.

9. Calibration (Barium)

9.1 Aspirate standard (*1*) in 6.6. With a minimum of scale expansion or burner rotation, obtain a reading of 0.5 ± 0.1 on the absorbance meter or alternative read-out device.

9.2 Aspirate the standards of 6.6 sequentially into the flame and record the output (or note the meter deflections). Aspirate the solvent alone after each standard.

9.3 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 absorbance 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.

9.4 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.

9.5 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.

9.6 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.

10. Procedure (Barium)

10.1 Weigh the sample to three significant figures into a 60-mL (2-oz) bottle. The sample mass is chosen to give an absorbance reading of 0.2 to 0.5. Add base oil to make 0.25 ± 0.01 g total mass. Add 50 mL of potassium suppressant solution, see 6.5, and dissolve. The maximum sample size to be used is 0.25 g, and the minimum is 0.05 g.

10.1.1 To hazy samples add 0.25 ± 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.

10.2 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 10.1.

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

11. Calculation (Barium)

11.1 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.

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

$$\text{Barium, \% mass} = \frac{CD}{10W} \tag{1}$$

where:

W = grams of sample/50 mL,
C = milligrams of metal/50 mL, and
D = dilution factor if dilution was necessary in 10.2.

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

12. Calcium Determination

12.1 Repeat Sections 7 through 10 replacing references made to barium with calcium using the following conditions:

12.1.1 Acetylene/nitrous oxide flame,

12.1.2 Calcium hollow cathode lamp, and

12.1.3 Analytical line 422.7 nm.

13. Magnesium Determination

13.1 Repeat Sections 7 through 10 replacing references made to barium with magnesium using the following conditions:

13.1.1 Acetylene/nitrous oxide flame,
13.1.2 Magnesium hollow cathode lamp, and
13.1.3 Analytical line 285.2 nm.

14. Zinc Determination

14.1 Repeat Sections 7 through 10 replacing references made to barium with zinc using the following conditions:
14.1.1 Acetylene/nitrous oxide flame,
14.1.2 Zinc hollow cathode lamp, and
14.1.3 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. 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.

15. Report

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

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

15.3 Concentrations less than the lower limits in 15.2 shall be reported as less than the appropriate lower limit.

16. Quality Control

16.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (see 6.7).

16.1.1 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.

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

TABLE 1 Repeatability

Element	Range, Mass %	Repeatability
Barium	0.005–1.0	$0.0478x^{2/3}$
Calcium	0.002–0.3	$0.0227x^{2/3}$
Magnesium	0.002–0.3	$0.0168x^{2/3}$
Zinc	0.002–0.2	$0.0247X^{2/3}$
Calcium	1.7	0.032
Zinc	1.0	0.025

TABLE 2 Reproducibility

Element	Range, Mass %	Reproducibility
Barium	0.005–1.0	$0.182x^{2/3}$
Calcium	0.002–0.3	$0.0779x^{2/3}$
Magnesium	0.002–0.3	$0.0705x^{2/3}$
Zinc	0.002–0.2	$0.0537X^{2/3}$
Calcium	1.7	0.090
Zinc	1.0	0.048

17. Precision and Bias

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

17.1.1 *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 1 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 this test method, exceed the values in Table 2 only in one case in twenty.

NOTE 11—The values of these precision estimates for selected values of x are set out in Table 3.

NOTE 12—The precision data in Section 17 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.

17.2 *Bias*:

17.2.1 No bias statement can be written because of the lack of suitable reference materials of known composition.

17.2.2 The presence of certain viscosity index improvers can cause a negative bias for one or more elements. In interlaboratory studies, this bias was found to be small relative to the reproducibility of this test method, and the bias was minimized by using smaller sample sizes (for example, a sample size of 0.050 g of a blended oil) for oils that contain viscosity index improvers.

18. Keywords

18.1 additive elements; atomic absorption spectrometry; barium; calcium; lubricating oils; magnesium; zinc

TABLE 3 Repeatability and Reproducibility

Mass % (x)	Repeatability	Reproducibility
Barium	$0.0487x^{2/3}$	$0.182\ x^{2/3}$
0.01	0.002	0.008
0.05	0.007	0.025
0.10	0.011	0.039
0.50	0.031	0.115
1.0	0.049	0.182
Calcium	$0.0227x^{2/3}$	$0.0779x^{2/3}$
0.002	0.0004	0.0012
0.01	0.001	0.004
0.05	0.003	0.011
0.3	0.010	0.035
Magnesium	$0.0168x^{2/3}$	$0.0705x^{2/3}$
0.002	0.0003	0.011
0.01	0.001	0.003
0.05	0.002	0.009
0.3	0.008	0.032
Zinc	$0.0247x^{2/3}$	$0.0537x^{2/3}$
0.002	0.0004	0.0009
0.01	0.001	0.002
0.05	0.003	0.007
0.20	0.008	0.018

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL MONITORING

X1.1 Confirm the performance of the instrument or the test procedure by analyzing quality control (QC) sample(s).

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practice D 6299).[4]

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D 6299).[4,5] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM method precision to ensure data quality (see Practice D 6299).[4]

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

X1.6 See Footnotes 4 and 5 for further guidance on QC and Control Charting techniques.

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[4] *ASTM MNL 7: Manual on Presentation of Data Control Chart Analysis*, 6th Ed., ASTM International, W. Conshohocken, PA, Section 3.

[5] In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 4628–97) that may impact the use of this standard.

(1) Added a QC sample to Section 6, Reagents.

(2) Added a QC section to Section 16.

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