Designation: D4628 – 16

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 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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in 3.1, 6.3, and 8.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

3. Summary of Test Method

3.1 A sample is weighed and base oil is added to 0.25 g ± 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.)

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.

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

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.

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. A 100 neutral oil which provides good solvency for

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[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] 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

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.

6.3 *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 attapulgus 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 16 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 volume % saturates, 0.1 volume % olefins, and a maximum of 3.2 volume % aromatics. If the kerosene used by an operator deviates appreciably from this composition, there may be significant error.

6.4 *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 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 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.

6.6 *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 6.4) 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 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 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 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

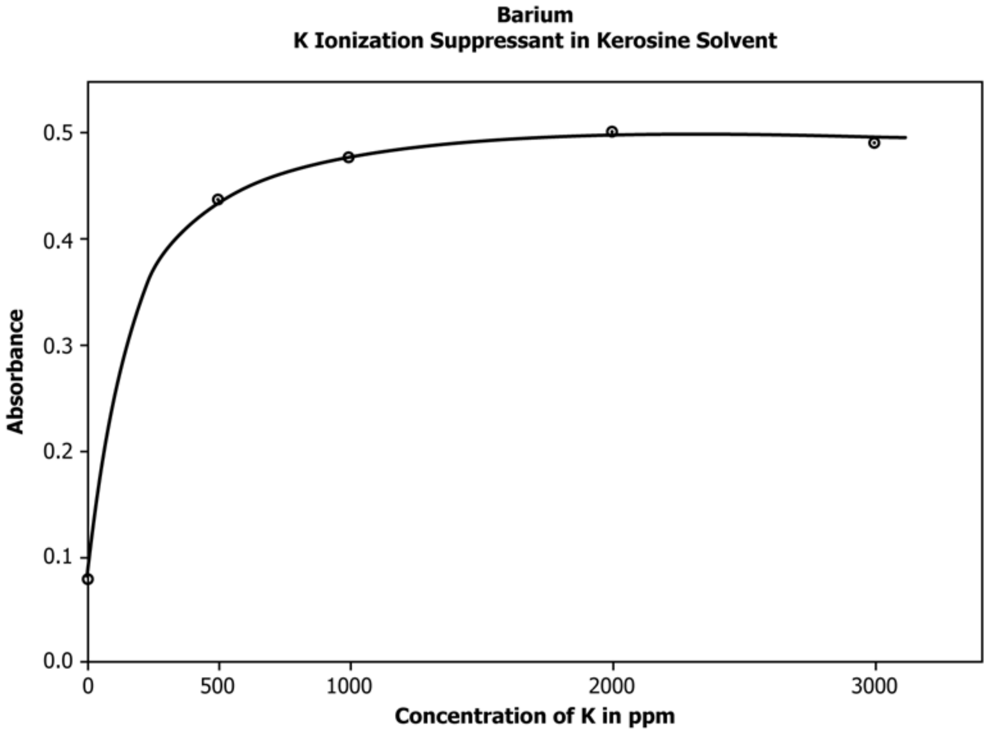

FIG. 1 Plot Graphs for Barium and Calcium

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 readout 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 bottle. The sample mass is chosen to give an absorbance reading of 0.2 to 0.5. Add base oil to make 0.25 g ± 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 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.

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 % to 0.1 % barium and 0.002 % to 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.

TABLE 2 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

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.

17. Precision and Bias[3]

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 2 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 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 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

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1207.

TABLE 3 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

TABLE 4 Repeatability and Reproducibility

Mass % (x)	Repeatability	Reproducibility
Barium	$0.0487\ x^{2/3}$	$0.182\ x^{2/3}$
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	$0.0227\ x^{2/3}$	$0.0779\ x^{2/3}$
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	$0.0168\ x^{2/3}$	$0.0705\ x^{2/3}$
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	$0.0247\ x^{2/3}$	$0.0537\ x^{2/3}$
0.002	0.0004	0.0009
0.01	0.001	0.002
0.05	0.003	0.007
0.20	0.008	0.018

APPENDIXES

(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 D6299).[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 D6299).[4] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

NOTE X1.1—In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

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 D6299).[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 Footnote 4 and Note X1.1 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.

X2. HELPFUL HINTS FOR OPERATION OF THE TEST METHOD D4628 TEST

X2.1 Many lubricating oils contain viscosity index (VI) improvers and may give low results when calibrations are performed using calibration standards that do not contain the VI improvers.

X2.1.1 The VI improver effect may be eliminated by using either a very large sample dilution or by adding the same VI improver to the calibration standards. The latter approach would usually be impractical, since for unknown samples, the laboratory would not know the type or the concentration of the VI improver present, if any.

X2.2 Standardize the instrument each time the flame is ignited. Carry out calibration 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 period of times from such causes as buildup of deposits on the burner slot or in the nebulizer.

X2.3 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.

X2.4 The visual appearance of the flame serves as a useful check to detect changes of condition.

X2.5 Low level working calibration standards should be prepared fresh daily from higher concentration (for example, 500 mg⁄kg or 1000 mg⁄kg) stock solutions.

X2.6 Always run a blank with all solvents and other reagents added to the standards and the samples.

X2.7 Whenever possible, employ background subtraction to obtain more reliable results.

X2.8 To avoid flame transport problems, add a metal-free base oil of about 4 cSt at 100 °C to both samples and calibration standards. A 100 neutral base oil is suitable. Avoid highly paraffinic oils.

X2.9 Standard addition technique may be employed for samples known to have elemental or other interferences.

X2.10 For best results, use a bracketing technique for calibration. This involves taking absorbance readings for the calibration solutions before and after each of the sample solutions.

X2.11 Employ adequate mixing and sampling procedures, especially for heavy oils. Heat heavy oils sufficiently to obtain good liquidity, and then shake vigorously on a shaking machine.

X2.12 Use the analytical wavelengths specified in the test method for measurements, because they have been established by experiment to be the optimum wavelengths and free from spectral interferences.

X2.13 Disassemble and clean the burner on a maintenance schedule that is appropriate to frequency and type of use.

X2.14 Inspect the nebulizer tubing daily for kinks or cracks, and replace as necessary.

X2.15 Measure the nebulizer uptake rate daily to check for plugging. Clean it if the rate is not normal.

X2.16 Adjust for variations due to buildup of deposits on the burner or the nebulizer during the course of determinations by frequently nebulizing the check standard.

X2.17 Adjust the gas flow rates when using the nitrous oxide/acetylene flame to minimize the carbon buildup on the burner. Clean off the carbon regularly during analysis with a sharp instrument. Carbon buildup can be particularly troublesome when nebulizing the organic solutions.

X2.18 Prevent leakage of acetone from the acetylene gas tank by monitoring the pressure. Replace the tank when the pressure reaches 50 psi.

X2.19 Check the alignment of the hollow cathode lamps before analysis, following the manufacturer's instructions.

X2.20 Clean all apparatus, glassware, etc. to prevent contamination. Soak the glassware in warm dilute (5 %) nitric acid for several hours, and then rinse thoroughly with deionized water.

X2.21 Verify the linearity of the concentrations/absorbance response for each analyte following the instrument manufacturer's instructions. Perform all determinations within this range. Prepare the standard solutions with concentrations at the top of the linear range.

X2.22 Match the matrix of standard solutions to sample solutions as closely as possible.

X2.23 Use pure, analyte-free solvents. Test Method D4628 recommends Baker "kerosene" (deodorized). Verify that the solvents are free of the analyte.

X2.24 Add ionization suppressant to all applicable solutions (standards and samples) using the recommended concentration as a guide. Determine the proper concentration by experiment using the instructions in this test method. Add the same concentration of ionization suppressant to all standard and sample solutions, and maintain these concentrations when the solutions are diluted.

X2.25 Keep all absorbances within the linear and calibration ranges. Dilute the sample solutions gravimetrically, if necessary.

X2.26 Since checking the absorbance of a sample is very quick once the instrument is calibrated, but changing the wavelength settings and hollow cathode lamps takes longer time, it is most economical to make measurements at a single wavelength on a series of samples and standards before changing conditions for a different analyte measurement.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D4628 – 14) that may impact the use of this standard. (Approved Dec. 1, 2016.)

(1) Deleted former footnote 3.

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