Designation: D6443 – 04

# Standard Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive X-ray Fluorescence Spectrometry (Mathematical Correction Procedure)[1]

This standard is issued under the fixed designation D6443; 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.

## 1. Scope*

1.1 This test method covers the determination of calcium, chlorine, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils, additives, and additive packages by wavelength dispersive X-ray fluorescence spectrometry. Matrix effects are handled with mathematical corrections.

1.2 For each element, the upper limit of the concentration range covered by this test method is defined by the highest concentration listed in Table 1. Samples containing higher concentrations can be analyzed following dilution.

1.3 For each element, the lower limit of the concentration range covered by this test method can be estimated by the limit of detection (LOD)[2] (see also 40 CFR 136 Appendix B) or limit of quantification (LOQ),[2] both of which can be estimated from $S_r$, the repeatability standard deviation. LOD and LOQ values, determined from results obtained in the interlaboratory study on precision, are listed in Table 2.

1.3.1 LOD and LOQ are not intrinsic constants of this test method. LOD and LOQ depend upon the precision attainable by a laboratory when using this test method.

1.4 This test method uses regression software to determine calibration parameters, which can include influence coefficients (that is, interelement effect coefficients) (Guide E1361), herein referenced as alphas. Alphas can also be determined from theory using relevant software.

1.5 Setup of this test method is intended for persons trained in the practice of X-ray spectrometry. Following setup, this test method can be used routinely.

1.6 The values stated in either SI units or angstrom units are to be regarded separately as standard.

1.7 *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.*

**TABLE 1 Calibration Standard Compositions, Concentrations in Mass %**

| Std. No. | Ca | Cl | Cu | Mg | P | S | Zn |
|---|---|---|---|---|---|---|---|
| 1 | 0.02 | 0.02 | 0.01 | 0.20 | 0.25 | 1.00 | 0.02 |
| 2 | 0.02 | 0.02 | 0.05 | 0.20 | 0.02 | 0.02 | 0.25 |
| 3 | 0.02 | 0.20 | 0.01 | 0.05 | 0.25 | 0.02 | 0.25 |
| 4 | 0.02 | 0.20 | 0.05 | 0.05 | 0.02 | 1.00 | 0.02 |
| 5 | 0.40 | 0.02 | 0.01 | 0.05 | 0.02 | 1.00 | 0.25 |
| 6 | 0.40 | 0.02 | 0.05 | 0.05 | 0.25 | 0.02 | 0.02 |
| 7 | 0.40 | 0.20 | 0.01 | 0.20 | 0.02 | 0.02 | 0.02 |
| 8 | 0.40 | 0.20 | 0.05 | 0.20 | 0.25 | 1.00 | 0.25 |
| 9 | 0.20 | 0.10 | 0.03 | 0.10 | 0.10 | 0.50 | 0.10 |
| 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

## 2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry

D4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy

D4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

[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] *Analytical Chemistry*, Vol 55, pp. 2210-2218.

[3] 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 2 Estimated LOD and LOQ, Units are Mass %**

| | Ca | Cl | Cu | Mg | P | Zn |
|---|---|---|---|---|---|---|
| LOD | 0.0002 | 0.0004 | 0.0002 | 0.0039 | 0.0006 | 0.0002 |
| LOQ | 0.0008 | 0.0015 | 0.0007 | 0.0130 | 0.0020 | 0.0007 |

D5185 Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in 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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis

2.2 *Government Standard:*[4]

40 CFR, 136 Appendix B, Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11, pp. 265-267

## 3. Summary of Test Method

3.1 The X-ray fluorescence spectrometer is initially calibrated by the following procedure. For each element, the slope and intercept of the calibration curve are determined by regressing concentration data and intensities measured on a set of physical standards. Empirical alphas can also be determined by regression when the appropriate set of physical standards is used for calibration. Theoretical alphas, calculated with special software, can also be used. In addition, a combination of theoretical and empirical alphas can be used.

3.2 A sample is placed in the X-ray beam, and the intensities of the appropriate fluorescence lines are measured. A similar measurement is made at a wavelength offset from each fluorescence line in order to obtain a background correction. Enhancement or absorption of the X-ray fluorescence of an analyte by an interfering element in the sample can occur, and these effects can be handled in the data reduction by implementation of alphas. Concentrations of the analytes are determined by comparison of net signals against calibration curves, which include influence coefficients (that is, alphas) calculated from theory, empirical data, or a combination of theory and empirical data.

## 4. Significance and Use

4.1 Lubricating oils can be formulated with additives, which can act as detergents, anti-oxidants, anti-wear agents, and so forth. Some additives can contain one or more of calcium, copper, magnesium, phosphorus, sulfur, and zinc. This test method can be used to determine if the oils, additives, and additive packages meet specification with respect to content of these elements.

4.2 This test method can also be used to determine if lubricating oils, additives, and additive packages meet specification with respect to chlorine concentration. In this context, specification can refer to contamination.

4.3 This test method is not intended for use on samples that contain some component that significantly interferes with the analysis of the elements specified in the scope.

4.4 This test method can complement other test methods for lube oils and additives, including Test Methods D4628, D4927, D4951, and D5185.

## 5. Interferences

5.1 The additive elements can affect the magnitudes of the measured intensities for each analyte. In general, the X-radiation emitted by each analyte can be absorbed by the other elements. Also, the X-radiation emitted by an analyte can be enhanced by some other component. The magnitudes of the absorption and enhancement effects can be significant. However, implementation of accurately determined alphas in the set of calibration parameters can satisfactorily correct for absorption and enhancement effects, thereby making this test method quantitative.

5.2 Molybdenum lines can spectrally overlap lines of magnesium, phosphorus, sulfur, and chlorine. Lead lines can spectrally overlap sulfur. Thus, this test method cannot be applied if molybdenum or lead are present at significant concentrations and if accurate overlap corrections cannot be made.

5.3 When a large d-spacing diffraction structure containing silicon is used as the analyzing crystal, corrections for the fluorescence of silicon may be needed. Calcium X rays from sample specimens cause silicon to fluoresce. This silicon radiation contributes to fluctuations in the background for magnesium measurements. If the effect is significant, this interference may be treated as a line overlap due to calcium.

## 6. Apparatus

6.1 *X-ray Spectrometer*, equipped for detection of soft X-ray radiation in the range from 1 to 10 angstroms. For optimum sensitivity, the spectrometer is equipped with the following:

6.1.1 *X-ray Tube Source*, with chromium, rhodium, or scandium target. Scandium can be advantageous for sensitivity enhancement of the low atomic number analytes. Other targets may also be employed. Avoid spectral interferences from tube lines on the analyte lines.

6.1.2 *Helium*, purgeable optical path.

6.1.3 *Interchangeable Analyzer Crystals*, germanium, lithium fluoride ($LiF_{200}$), graphite, pentaerythritol (PE), or a 50 angstrom diffraction structure, or a combination thereof. Other suitable crystals can be used.

6.1.4 *Pulse-Height Analyzer.*

6.1.5 *Detector*, gas flow proportional, or tandem gas flow proportional and scintillation counter.

NOTE 1—A gas sealed proportional counter was used in the interlaboratory study on precision and was found to be satisfactory.

6.2 *Mixing Device Such as a Shaker, Ultrasonic Bath, or Vortex Mixer*, capable of handling from 30-mL to 1-L bottles.

[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

**TABLE 3 Calculated Repeatability (r) and Reproducibility (R) for Oils, Units are Mass %**

| | Ca | | Cl | | Cu | | Mg | | P | | S | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concn | r | R | r | R | r | R | r | R | r | R | r | R | r | R |
| 0.0010 | 0.0003 | 0.0020 | 0.0003 | 0.0020 | 0.0002 | 0.0009 | | | 0.0002 | 0.0007 | | | 0.0001 | 0.0005 |
| 0.0030 | 0.0004 | 0.0029 | 0.0004 | 0.0021 | 0.0003 | 0.0012 | 0.0025 | 0.0081 | 0.0004 | 0.0016 | | | 0.0002 | 0.0012 |
| 0.0100 | 0.0007 | 0.0049 | 0.0007 | 0.0025 | 0.0004 | 0.0018 | 0.0036 | 0.0115 | 0.0008 | 0.0036 | | | 0.0005 | 0.0027 |
| 0.0300 | 0.0012 | 0.0083 | 0.0014 | 0.0036 | 0.0006 | 0.0027 | 0.0051 | 0.0163 | 0.0018 | 0.0078 | 0.0010 | 0.0069 | 0.0011 | 0.0058 |
| 0.1000 | 0.0022 | 0.0151 | | | | | 0.0075 | 0.0243 | 0.0042 | 0.0182 | 0.0030 | 0.0204 | 0.0024 | 0.0134 |
| 0.2000 | 0.0031 | 0.0213 | | | | | 0.0094 | 0.0305 | 0.0069 | 0.0295 | 0.0056 | 0.0381 | 0.0040 | 0.0218 |
| 0.4000 | | | | | | | | | | | 0.0104 | 0.0711 | | |
| 0.8000 | | | | | | | | | | | 0.0194 | 0.1328 | | |

6.3 *X-ray Disposable Plastic Cells*, with suitable film window. Suitable films can include polyester, polypropylene, or polyimide. A film thickness of 4 µm is preferred. Avoid using film that contains any of the analytes.

## 7. Reagents and Materials

7.1 *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.[5] Other grades can 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.

7.2 *Helium*, preferably ultrahigh purity (at least 99.95 %), for optical path of spectrometer.

7.3 *P-10 Ionization Gas*, 90 volume % argon and 10 volume % methane for the flow proportional counter.

NOTE 2—P-10 gas was used in the interlaboratory study on precision. Other satisfactory gases or gas mixtures can be applicable.

7.4 *Dilution Solvent*, a hydrocarbon solvent, which does not contain a detectable amount of any analyte. U.S.P. white (mineral) oil has been found to be satisfactory.

7.5 *Calibration Standard Materials*:

7.5.1 *Concentrated Solutions of Oil-soluble Compounds*, each containing one of the following: calcium, copper, magnesium, phosphorus, or zinc.

7.5.1.1 Some commercially available oil-soluble standard materials are prepared from sulfonates and therefore contain sulfur. To use these materials for preparation of the calibration standard blends, it is necessary to know their sulfur concentrations. Test Method D1552, or other appropriate methods, can be used to determine sulfur content.

7.5.1.2 Secondary standards, such as those prepared from petroleum additives, for example, can also be used if their use does not affect the analytical results by more than the repeatability of this test method.

7.5.2 *Di-n-butyl Sulfide*, a high-purity standard with a certified analysis for total sulfur content.

NOTE 3—Di-n-butyl sulfide is flammable and toxic.

7.5.3 *Oil-soluble Chlorine-containing Compound*, a high purity standard with a certified analysis for total chlorine content.

7.5.4 *Stabilizers*, Stabilizers can be used to ensure uniformity of the calibration standard blends. Use stabilizers that do not contain a detectable amount of any analyte.

## 8. Sampling and Sample Handling

8.1 Take samples in accordance with the instructions in Practice D4057 or D4177, when applicable.

8.2 Mix well samples and calibration standard blends before introduction into the X-ray instrument.

## 9. Preparation of Calibration Standards

9.1 Prepare calibration standard blends by accurate dilution of the oil-soluble standard solutions with the dilution solvent. These blends (Practice D4307), with accurately known analyte concentrations, shall approximate the nominal values listed in Table 1.

9.1.1 When empirical alphas are determined by regression, prepare and measure all standard blends listed in Table 1.

9.1.2 When theoretical alphas are used, a subset of the standard blends (for example, standards 2, 6, 8, and 10) can be satisfactory.

9.2 *Drift Correction Monitors (Optional)*—The use of drift correction monitors for determination and correction of instrument drift can be advantageous. Monitors are stable, solid disks or pellets containing all elements covered by this test method. Two disks are preferred to correct for both sensitivity and base line drifts. The high-concentration drift monitor provides high-count rates, so that for each analyte, counting error is less than 0.25 % relative. The low-concentration drift monitor provides low-count rates, so that for each element, count rate is similar to that obtained with the calibration blank, or zero mass % standard.

## 10. Calibration

10.1 For the Kα-spectral line for each analyte, assemble a channel per operating instructions of the X-ray instrument. Suggested, approximate instrument settings are listed in Table 5. Actual settings can be instrument dependent; hence, the information in Table 5 is for guidance only.

10.2 For correct operation of the X-ray instrument, assemble the required measurement program, calculation program, and monitor program (when drift correction monitors are implemented), as appropriate.

10.3 When drift correction monitors are implemented, measure monitor intensities for each analyte.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.

**TABLE 4 Repeatability and Reproducibility for Additives, Units are Mass %**

NOTE—$X$ = concentration in mass %.

| Analyte | Concn(s) | Repeatability | Reproducibility |
|---|---|---|---|
| Ca | 1.00 - 1.50 | 0.0226 | 0.1151 |
| Cl | 0.070 | 0.0039 | 0.0104 |
| Mg | 0.30 - 1.00 | 0.0721 | 0.1797 |
| P | 0.30 - 1.50 | $0.02448\ X^{0.8}$ | $0.1663\ X^{0.8}$ |
| S | 1.00 - 5.00 | $0.02783\ X^{0.8}$ | $0.1744\ X^{0.8}$ |
| Zn | 0.30 - 1.50 | $0.02002\ X^{1.08}$ | $0.1183\ X^{1.08}$ |

10.4 Fill, to at least three-fourths full, X-ray sample cells with calibration standard blends, and ensure that the film is flat with no wrinkles or bulges. Punch a vent hole in the top of the cell. Introduce the calibration standard blends into the X-ray instrument in random order, and for each analyte, measure X-ray intensities. In general, a total count time of about 4 to 5 min per sample is typical. Common background measurement for two or more analytes can be used. If a standard must be remeasured, use a fresh aliquot, a fresh cup, and a new piece of film.

10.4.1 Measure magnesium and chlorine intensities first because they will be most sensitive to changes in the sample cell configuration.

10.5 Following measurement of the calibration standard blends, for each analyte, regress the concentration data with measured intensity data. Typically, the model describing the concentration-intensity relationship is:

$$C_i = (D_i + E_i I_i)\,(1 + \Sigma_j \alpha_{ij} C_j) \quad (1)$$

where:

$C_i$ = concentration of the analyte element $i$,
$D_i$ = intercept of the calibration curve for element $i$,
$E_i$ = slope of the calibration curve for element $i$,
$I_i$ = net measured intensity for element $i$,
$\alpha_{ij}$ = influence coefficient for the effect of each absorbing element $j$ on analyte element $i$, and
$C_j$ = concentration of interfering element $j$.

10.5.1 When empirical alphas are used exclusively, the complete set of calibration standards (see Table 1) is measured. Then, for each analyte in turn, regression software is used to determine the $D$ value, the $E$ value, and also the relevant alphas.

10.5.1.1 Experimental results indicate that the calibration for magnesium does not require alphas because interelement effects on magnesium are not significant. Because of limited magnesium sensitivity on many X-ray instruments, empirically determined alphas can often be unrealistic and problematic.

10.5.1.2 Experimental results indicate that for each analyte, an alpha for the effect of copper can be ignored because the maximum copper concentration covered by this test method is only 0.05 mass %. When copper alphas are determined empirically, they can often be unrealistic and problematic.

10.5.2 When theoretical alphas are used exclusively, a subset of the calibration standard blends (see Table 1, typically standards 2, 6, 8, and 10) can be measured. Then, for each element in turn, the theoretical alphas are edited into the calibration parameter list, and the $D$ value and $E$ value are determined by regression.

10.5.3 When a mix of empirical and theoretical alphas is used, the complete set of calibration standards (see Table 1) is measured. Then, for each element in turn, the relevant theoretical alphas are edited into the calibration parameter list and the $D$ value, the $E$ value, and remaining alphas (if any) are determined by regression.

10.6 Typically, the initial calibration to obtain the slope, intercept, and alphas is performed only once. Subsequent recalibration is performed with two standards (typically, the drift correction monitors) in order to correct for changes in X-ray sensitivity and blank. The two standards are chosen such that they span the range of expected concentrations for the unknown samples.

## 11. Analysis

11.1 Fit sample cells with film, ensuring that there are no wrinkles or bulges. Fill the cell with sample, to at least three-fourths full. Punch a vent hole in the top of the cell.

11.2 Measure intensities in the same manner as with the calibration standards.

11.3 The analyte concentrations for each sample are calculated from the measured intensities, $D$ values, $E$ values, and alphas, using a model such as Eq 1.

11.4 When a sample contains an analyte at a concentration greater than the corresponding maximum concentration listed in Table 1, dilute the sample appropriately and re-analyze.

## 12. Quality Control (Required)

12.1 Typically, one or more stable, quality control (QC) samples that are similar in composition to test samples are analyzed regularly by the testing laboratory. Because data quality requirements can vary among testing laboratories, individual laboratories can determine the frequency of QC sample analysis and the acceptable control limits. Appendix X2 provides additional guidance with respect to quality control monitoring.

12.2 When QC results are not within control limits, carry out corrective action, such as drift correction or recalibration, or both.

12.3 The QC sample precision can be compared with precision of this test method to determine data quality.

## 13. Reporting

13.1 For samples that required dilution, multiply results by the dilution factor.

13.2 Report results in mass %, using three significant figures for concentrations greater than 0.0100 %, two significant figures for concentrations between 0.0010 % and 0.0100 %, and one significant figure for concentrations below 0.0010 %.

13.3 For guidance in rounding significant figures, refer to Practice E29.

13.4 Report results that are below the limit of detection as *not detected* or *less than*, followed by the LOD value. The value assigned to LOD can be the appropriate value listed in Table 2, or a value, characteristic of an individual laboratory's performance, determined with the same methodology used in Table 2, or some plausible value mutually accepted by interested participants.

**TABLE 5 Suggested Channel Settings**

| Analyte | kV, mA | Crystal | Collimator | Detector, Flow, Scintillation, Both | Peak, Bkgd Angles, Degrees 2 theta |
|---|---|---|---|---|---|
| Ca | 40, 70 | LiF(200) | Coarse, 0.70 mm | Flow | 113.16, 116.16 |
| Cl | 40, 70 | Ge | Coarse, 0.70 mm | Flow | 92.80, 94.80 |
| Cu | 45, 60 | LiF(200) | Fine, Inter., 0.30 mm | Both | 45.03, 47.03 |
| Mg | 40, 70 | Synthetic multilayer, 50 angstroms | Coarse, 0.70 mm | Flow | 23.05, 25.80 |
| P | 40, 70 | Ge | Coarse, 0.70 mm | Flow | 141.00, 137.00 |
| S | 40, 70 | Ge | Coarse, 0.70 mm | Flow | 110.75, 116.75 |
| Zn | 45, 60 | LiF(200) | Fine, Inter., 0.30 mm | Both | 41.76, 47.03 |

**TABLE 6 Calculated Repeatability (r) and Reproducibility (R) for Additives, Units are Mass %**

| | Ca | | Cl | | Mg | | P | | S | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concn | r | R | r | R | r | R | r | R | r | R | r | R |
| 0.070 | | | 0.0039 | 0.0104 | | | | | | | | |
| 0.300 | | | | | 0.072 | 0.180 | 0.009 | 0.063 | | | 0.005 | 0.032 |
| 0.700 | | | | | 0.072 | 0.180 | 0.018 | 0.125 | | | 0.014 | 0.080 |
| 1.00 | 0.0226 | 0.1151 | | | 0.072 | 0.180 | 0.024 | 0.166 | 0.028 | 0.174 | 0.020 | 0.118 |
| 1.50 | 0.0226 | 0.1151 | | | | | 0.034 | 0.230 | 0.038 | 0.241 | 0.031 | 0.183 |
| 3.00 | | | | | | | | | 0.067 | 0.420 | | |
| 5.00 | | | | | | | | | 0.101 | 0.632 | | |

**TABLE 7 Bias Estimation, Units are Mass %**

| Analyte | Oil G | | | | Oil J | | | |
|---|---|---|---|---|---|---|---|---|
| | Known | Mean | Apparent Bias | Significant? | Known | Mean | Apparent Bias | Significant? |
| Ca | 0.0024 | 0.0025 | 0.0001 | no | 0.1303 | 0.1320 | 0.0017 | no |
| Cu | 0.0023 | 0.0024 | 0.0001 | no | 0.0143 | 0.0147 | 0.0004 | no |
| Mg | 0.0103 | 0.0110 | 0.0007 | no | 0.1103 | 0.1094 | –0.0009 | no |
| P | 0.0026 | 0.0025 | –0.0001 | no | 0.1487 | 0.1511 | 0.0024 | no |
| Zn | 0.0023 | 0.0025 | 0.0002 | no | 0.1362 | 0.1347 | –0.0015 | no |

13.4.1 For samples that require dilution, the appropriate limit of detection is the limit of detection determined for the diluted specimen multiplied by the sample dilution factor.

## 14. Precision and Bias [6]

14.1 The precision of this test method was determined by statistical analysis of interlaboratory results. In this study, nine laboratories analyzed eleven oils and three additives in duplicate. To estimate bias, two of the oils were lab synthesized using Conostan standards.[7,8] Six labs used theoretical alphas exclusively, two labs used a combination of theoretical and empirical, and one lab used empirical alphas exclusively. A variety of oil soluble standards was used by the laboratories participating in the interlaboratory study. The ranges of analyte concentrations together with their precisions are listed below.

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Tables 8-6 in only one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Tables 8-6 in only one case in twenty.

14.2 *Bias*—An indication of bias was determined from interlaboratory study results obtained on two different laboratory synthesized oils. One lab blend (Oil G) was prepared by combining Conostan 5000 ppm standards (Ca, Zn, Cu, P), Conostan concentrate (Mg), 2-chloro-paraxylene,[8,9] base oil, and mineral oil.[8,9] The following concentrations were considered known: Ca, 0.0024 %; Zn, 0.0023 %; Cu, 0.0023 %; P, 0.0026 %; Mg, 0.0103 %; Cl, 0.0035 %. Similarly, a second lab blend (Oil J) was prepared by combining Conostan concentrates (Zn, P, Ca, Mg), Conostan 5000 ppm (Cu), 2-chloro-paraxylene, and mineral oil. The following concentrations were considered known: Ca, 0.1303 %; P, 0.1487 %; Zn, 0.1362 %; Mg, 0.1103 %; Cu, 0.0143 %; Cl, 0.0275 %. For these two blends, Table 7 summarizes interlaboratory results as they pertain to bias.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1450.

[7] The sole source of supply of the Conostan Standards known to the committee at this time is ConocoPhillips Inc., CONOSTAN Division, 1000 South Pine, Ponca City, OK 74602.

[8] If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[9] The sole source of supply known to the committee at this time is Aldrich Chemical Co., 1001 West Saint Paul Ave., Milwaukee, WI 53233.

**TABLE 8 Repeatability and Reproducibility for Oils, Units are Mass %**

NOTE—$X$ = concentration in mass %.

| Analyte | Concns | Repeatability | Reproducibility |
|---|---|---|---|
| Ca | 0.001 - 0.200 | $0.006914\ (X+0.0007)^{0.5}$ | $0.04762\ (X+0.0007)^{0.5}$ |
| Cl | 0.001 - 0.030 | $0.0356\ (X+0.0086)$ | $0.05612\ (X+0.0340)$ |
| Cu | 0.001 - 0.030 | $0.002267\ (X+0.0013)^{0.4}$ | $0.01068\ (X+0.0013)^{0.4}$ |
| Mg | 0.003 - 0.200 | $0.01611\ (X+0.0008)^{0.333}$ | $0.05208\ (X+0.0008)^{0.333}$ |
| P | 0.001 - 0.200 | $0.02114\ X^{0.7}$ | $0.09112\ X^{0.7}$ |
| S | 0.030 - 0.800 | $0.02371\ X^{0.9}$ | $0.1623\ X^{0.9}$ |
| Zn | 0.001 - 0.200 | $0.01225\ X^{0.7}$ | $0.06736\ X^{0.7}$ |

14.2.1 Sulfur was not included in the bias estimation because some of the components used to blend the oils contained sulfur at uncertified concentrations.

14.2.2 Chlorine was not included in the bias estimation because contamination was suspected.

14.3 *Limit of Detection and Limit of Quantification*—The LOD and LOQ determined from data from the interlaboratory study on precision are listed in Table 2. The LOD is herein defined as three times $S_r$, and the LOQ is herein defined as ten times $S_r$, where $S_r$ is the pooled repeatability standard deviation determined at concentration(s) less than approximately five times the estimated limit of detection[2] (see also 40 CFR 136 Appendix B).

14.3.1 LOD and LOQ values for sulfur were not estimated because the sulfur concentrations in the interlaboratory study samples were too high.

## 15. Keywords

15.1 additive elements; additives; calcium; chlorine; copper; lubricating oils; magnesium; phosphorus; sulfur; wavelength dispersive X-ray spectrometry; zinc

# APPENDIXES

**(Nonmandatory Information)**

## X1. AIDS TO THE ANALYST

X1.1 In accordance with regulations governing the use of ionizing radiation, provide training to all personnel authorized to operate the X-ray instrument. Provide finger and body radiation detection badges for operators. Do not disable any of the X-ray instrument's safety features.

X1.2 Use appropriate sample storage and mixing procedures. When analyzing additives and additive packages by dilution, ensure satisfactory mixing of the diluted sample.

X1.3 Use the peak and background wavelengths (angles) specified in the test method because they have been found satisfactory by experimentation.

X1.4 Determine if the sample cell film contains a significant concentration of any analyte (typically, indicated by the $D$ value in the concentration-intensity model, Eq 1). Avoid using film that contains a significant concentration of an analyte.

X1.5 Determine the integrity of the sample cell film when it is in contact with sample. Some sample types can dissolve certain types of film. Analyze samples as soon as possible after filling the sample cells.

X1.6 Avoid contamination of the sample cells by touching the inside of the cell or the film.

X1.7 Avoid using sample cells when the attached film wrinkles or bulges.

X1.8 Punch a vent hole in the top of a filled sample cell.

X1.9 When a new container or batch of sample cell film is used, check all calibration curves.

X1.10 Confirm the absence of analytes in diluents and stabilizers. For preparation of calibration standards, use reagent grade chemicals with certified concentrations of the relevant analytes.

X1.11 Obtain sufficient quantities of quality control samples for each type of sample analyzed (for example, an automotive lube oil, an additive package, and so forth). Ensure that these quality control samples will remain uniform for a reasonable period (typically, one year). If such samples are not available, synthesize QC samples from oil-soluble standards.

X1.12 For each QC sample, define a frequency of analysis and control limits. Implement this QC protocol.

X1.13 Establish a list of corrective actions that can be implemented when results from a QC analysis are outside control limits.

X1.14 Prepare or obtain solid pellets (for example, glass, fused lithium tetraborate, plastic, and so forth) containing the various analytes. These pellets can serve as monitors to determine and correct drift caused by performance changes in the X-ray instrument.

X1.15 Analyze U.S.P. white (mineral) oil, which can serve as a blank. Results obtained on a blank can be subtracted from sample results to correct for film impurities and drift in the calibration intercept.

## X2. QUALITY CONTROL (QC) MONITORING

X2.1 Confirm the performance of the instrument or the test procedure by analyzing QC sample(s).

X2.2 Prior to monitoring the measurement process, the user of this test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL7[10]).

X2.3 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 Note X2.1). Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

NOTE X2.1—In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

X2.4 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 test method precision to ensure data quality (see Practice D6299 and MNL7[10]).

X2.5 It is recommended, if possible, that 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 this shall be homogenous and stable under the anticipated storage conditions.

X2.6 See Practice D6299 and MNL7[10] for further guidance on QC and control charting techniques.

[10] MNL7, *Manual on Presentation of Data Control Chart Analysis*, 6th Ed., Section 3, ASTM International, W. Conshohocken, PA 19428.

## SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D6443–99) that may impact the use of this standard.

*(1)* Updated 12.1.

*(2)* Added a new Appendix X2.