INTERNATIONAL

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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~~ 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.

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

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

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum ~~Products~~ Products, Liquid Fuels, and Lubricantsand is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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

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

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.*

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
D5185 Test Method for Multielement Determination of Used and Unused Lubricating Oils and 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 Several additive elements and their compounds are added to the lubricating oils to give beneficial performance (Table 3).

4.3 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.

4.4 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.

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[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.

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

TABLE 3 Lubricants and Additive Materials

Element	Compounds	Purpose/Application
Calcium	Sulfonates, phenates	Detergent inhibitors, dispersants
Chlorine	Trace contaminants, chlorinated cleaning solvents	Avoid servo-valve erosion, dewaxing compounds
Copper	Copper dithiophosphates	Anti-wear agent, anti-oxidant
Magnesium	Sulfonates, phenates	Detergent inhibitors
Phosphorus	dithiophosphates, phosphates phosphites	anti-rusting agents, extreme pressure additives, anti-wear
Sulfur	Base oils, sulfonates, thiophosphates, polysulfides and other sulfurized components	Detergents, extreme pressure additives, anti-wear
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

4.5 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.

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.

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[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 ~~3~~4 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		

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~~6. Actual settings can be instrument dependent; hence, the information in Table ~~5~~6 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.