Designation: D7040 – 04 (Reapproved 2015)

Standard Test Method for Determination of Low Levels of Phosphorus in ILSAC GF 4 and Similar Grade Engine Oils by Inductively Coupled Plasma Atomic Emission Spectrometry[1]

This standard is issued under the fixed designation D7040; 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 quantitative determination of phosphorus in unused lubricating oils, such as International Lubricant Standardization and Approval Committee (ILSAC) GF 4 and similar grade engine oils, by inductively coupled plasma atomic emission spectrometry.

1.2 The precision statements are valid for dilutions in which the mass % sample in solvent is held constant in the range of 1mass % to 5 mass % oil.

1.3 The precision tables define the concentration ranges covered in the interlaboratory study (500 mg/kg to 800 mg/kg). However, both lower and higher concentrations can be determined by this test method. The low concentration limits are dependent on the sensitivity of the ICP instrument and the dilution factor. The high concentration limits are determined by the product of the maximum concentration defined by the linear calibration curve and the sample dilution factor.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

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

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

3. Summary of Test Method

3.1 A sample portion is weighed and diluted by mass with mixed xylenes or other solvent. An internal standard, which is required, is either weighed separately into the test solution or is previously combined with the dilution solvent. Calibration standards are prepared similarly. The solutions are introduced to the ICP instrument by a peristaltic pump (required). By comparing emission intensity of phosphorus in the test specimen with emission intensities measured with the calibration standards and by applying the appropriate internal standard and background corrections, the concentrations of phosphorus in the sample is calculated.

4. Significance and Use

4.1 This test method usually requires several minutes per sample. Other test methods which can be used for the determination of phosphorus in lubricating oils include WDXRF Test Method D4927 and ICPAES Test Methods D4951 and D5185. However, this test method provides more precise results than Test Methods D4951 or D5185.

4.2 Lubricating oils are typically blends of additive packages, and their specifications are also determined, in part,

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

Current edition approved April 1, 2015. Published June 2015. Originally approved in 2004. Last previous edition approved in 2010 as D7040 – 04 (2010). DOI: 10.1520/D7040-04R15.

[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.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

Documents
Document Sharing Hub
Full document details: ASTM D7040-04(2015)

by elemental composition. This test method can be used to determine if unused lubricating oils meet specifications with respect to elemental composition.

4.3 It is expected that GF 4 grade engine oils marketed in the years 2004 to 2005 will have a maximum phosphorus concentration level of 500 mg/kg to 800 mg/kg. These limits are required to minimize poisoning of automotive emission control catalysts by volatile phosphorus species. It is anticipated that the later grades of oils may have even lower phosphorus levels.

5. Interferences

5.1 *Spectral*—There are no known spectral interferences between phosphorus and other elements covered by this test method when using the spectral lines 177.51 nm, 178.29 nm, 185.94 nm, 213.62 nm, 214.91 nm, or 253.40 nm for phosphorus. These wavelengths are only suggested and do not represent all possible choices. Wavelengths below 190 nm require a vacuum or inert gas purged optical path be used. However, if spectral interferences exist because of other interfering elements or selection of other spectral lines, correct for the interference using the technique described in Test Method D5185.

5.2 *Viscosity Index Improver Effect*—Viscosity index improvers, which can be present in multi-grade lubricating oils, can bias the measurements.[3] However, the biases can be reduced to negligible proportion by using the specified solvent-to-sample dilution and an internal standard.

6. Apparatus

6.1 *Inductively-Coupled Plasma Atomic Emission Spectrometer*—Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz ICP torch and r-f generator to form and sustain the plasma.

6.2 *Analytical Balance,* capable of weighing to 0.001 g or 0.0001 g, capacity of 150 g.

6.3 *Peristaltic Pump (Required)*—A peristaltic pump is required to provide a constant flow of solution. The pumping speed shall be in the range 0.5 mL/min to 3 mL/min. The pump tubing shall be able to withstand at least a 6 h exposure to the dilution solvent. Fluoroelastomer copolymer[4] tubing is recommended.

6.4 *Solvent Dispenser (Optional)*—A solvent dispenser calibrated to deliver the required weight of diluent can be advantageous. Ensure that solvent drip does not affect accuracy.

6.5 *Specimen Solution Containers,* of appropriate size, glass or polyolefin vials, or bottles with screw caps.

6.6 *Vortexer (Optional)*—Vortex the sample plus diluent mixture until the sample is completely dissolved.

6.7 *Ultrasonic Homogenizer (Optional)*—A bath-type or probe-type ultrasonic homogenizer can be used to homogenize the test specimen.

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]

7.2 *Base Oil,* U.S.P. white oil, or a lubricating base oil that is free of analytes, having a viscosity at room temperature as close as possible to that of the samples to be analyzed.

7.3 *Internal Standard (Required)*—An oil-soluble internal standard element is required. The following internal standards were successfully used in the interlaboratory study on precision: Co (most common), Sc, and Y. Other appropriate internal standards may also be used.

7.4 *Organometallic Standards*—Multi-element standards, containing known concentrations (approximately 0.1 mass %) of each element, can be prepared from the individual metal concentrates. Refer to Practice D4307 for a procedure for preparation of multi-component liquid blends. When preparing multi-element standards, be certain that proper mixing is achieved. Commercially available multi-element blends (with known concentrations of each element at approximately 0.1 mass %) are also satisfactory.

7.4.1 It can be advantageous to select concentrations that are typical of unused oils. However, it is imperative that concentrations are selected such that the emission intensities measured with the working standards can be measured precisely (that is, the emission intensities are significantly greater than background) and that these standards represent the linear region of the calibration curve. Frequently, the instrument manufacturer publishes guidelines for determining linear range.

7.4.2 Some commercially available organometallic standards are prepared from metal sulfonates and, therefore, contain sulfur.

7.4.3 Petroleum additives can also be used as organometallic standards if their use does not adversely affect precision nor introduce significant bias.

7.5 *Dilution Solvent*—Mixed xylenes, o-xylene, and kerosine were successfully used in the interlaboratory study on precision.

8. Internal Standardization (Required)

8.1 The internal standard procedure requires that every test solution (sample and standard) have the same concentration (or a known concentration) of an internal standard element that is not present in the original sample. The internal standard is usually combined with the dilution solvent. Internal standard

[3] Bansal, J. G., and McElroy, F. C., *SAE Paper 932694*, October 1993. Available from Society of Automotive Engineers (SAE), 400 Commonwealth Dr., Warrendale, PA 15096-0001.

[4] Fluoroelastomer copolymer is manufactured as Viton, a trademark owned by E. I. duPont de Nemours.

[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.

AVA Documents
Document Sharing Hub

Full document details: ASTM D7040-04(2015)