Designation: D7040 – 04

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.

This standard has been approved for use by agencies of the Department of Defense.

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 1 to 5 mass % oil.

1.3 The precision tables define the concentration ranges covered in the interlaboratory study (500 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 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

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.

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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] 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.

4.2 Lubricating oils are typically blends of additive packages, and their specifications are also determined, in part, 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 2004-2005 will have a maximum phosphorus concentration level of 500 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, 178.29, 185.94, 213.62, 214.91, 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 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 compensation is typically handled in one of two different ways, summarized as follows:

8.1.1 Calibration curves are based on the measured intensity of each analyte divided (that is, scaled) by the measured intensity of the internal standard per unit internal standard

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[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.

element concentration. Concentrations for each analyte in the test specimen solution are read directly from these calibration curves.

8.1.2 For each analyte and the internal standard element, calibration curves are based on measured (unscaled) intensities. Uncorrected concentrations for each analyte in the test specimen solution are read from these calibration curves. Corrected analyte concentrations are calculated by multiplying the uncorrected concentrations by a factor equal to the actual internal standard concentration divided by the uncorrected internal standard concentration determined by analysis.

8.2 Dissolve the organometallic compound representing the internal standard in dilution solvent and transfer to a dispensing vessel. The stability of this solution shall be monitored and prepared fresh (typically weekly) when the concentration of the internal standard element changes significantly. The concentration of internal standard element shall be at least 100 times its detection limit. A concentration in the range of 10 to 20 mg/kg is typical.

NOTE 1—This test method specifies that the internal standard is combined with the dilution solvent because this technique is common and efficient when preparing many samples. However, the internal standard can be added separately from the dilution solvent as long as the internal standard concentration is constant or accurately known.

9. Sampling

9.1 The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Thus, take laboratory samples in accordance with the instructions in Practice D4057. The specific sampling technique can affect the accuracy of this test method.

10. Preparation of Apparatus

10.1 *Instrument*—Design differences between instruments, ICP excitation sources, and different selected analytical wavelengths for individual spectrometers make it impractical to detail the operating conditions. Consult the manufacturer's instructions for operating the instrument with organic solvents. Set up the instrument for use with the particular dilution solvent chosen.

10.2 *Peristaltic Pump*—Inspect the pump tubing and replace it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

10.3 *ICP Excitation Source*—Initiate the plasma source at least 30 min before performing an analysis. During this warm-up period, nebulize the dilution solvent. Inspect the torch for carbon buildup during the warm-up period. If carbon buildup occurs, replace the torch immediately and consult the manufacturer's operating guide to take proper steps to remedy the situation.

NOTE 2—Carbon that accumulates on the tip of the torch injector tube can be removed by using nebulizer gas that consists of approximately 1 % oxygen in argon.

10.3.1 Generally, carbon buildup can be minimized by increasing the intermediate argon flow rate or lowering the torch, or both, relative to the load coil.

NOTE 3—Some manufacturers recommend even longer warm-up periods to minimize changes in the slopes of the calibration curves.

10.4 *Wavelength Profiling*—Perform any wavelength profiling that is specified in the normal operation of the instrument.

10.5 *Operating Parameters*—Assign the appropriate operating parameters to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (required), interelement correction factors (refer to 5.1), integration time, and internal standard compensation (required). Multiple integrations (typically three) are required for each measurement. A typical integration time is 10 s.

11. Preparation of Test Specimens

11.1 *Diluent*—Diluent refers to the dilution solvent containing the internal standard (refer to 8.2).

11.2 Test specimen solutions are prepared in the same way that calibration standards are prepared (refer to 12.2). The mass % oil in diluent shall be the same for calibration standards and test specimen solutions.

11.2.1 *Lubricating Oil Specimens*—Weigh appropriate amount of the test specimen to the nearest 0.001 g. The weight of the test specimen taken will vary depending upon the metal concentration of the specimen. Dilute by mass with the diluent. Mix well.

11.3 Record all weights and calculate dilution factors by dividing the sum of the weights of the diluent, sample, and base oil (if any) by the weight of the sample.

11.4 The user of this test method has the option of selecting the dilution factor, that is, the relative amounts of sample and diluent. However, the mass % sample in diluent (for calibration standards and test specimens) shall be constant throughout this test method, and the mass % sample in diluent shall be in the range of 1 to 5 mass %.

11.4.1 All references to dilute and diluting in this test method refer to the user-selected dilution.

11.5 *Blank*—Prepare a blank by diluting the base oil or white oil with the diluent.

11.6 *Working Standards*—Weigh to the nearest 0.001 g, approximately 1 to 3 g of each multi-element standard (refer to 7.4) into separate bottles. Dilute by mass with the diluent.

11.7 *Check Standard*—Prepare instrument check standards in the same manner as the working standards such that the concentrations of elements in the check standards are similar to the concentrations of elements in the test specimen solutions. It is advisable to prepare the check standard from alternative sources of certified organometallic standards.

12. Calibration

12.1 The linear range of all calibration curves shall be determined for the instrument being used. This is accomplished by running intermediate standards between the blank and the working standards and by running standards containing higher concentrations than the working standards. Analyses of test specimen solutions shall be performed within the linear range of the calibration curve.

12.2 At the beginning of the analysis of each set of test specimen solutions, perform a two-point calibration using the blank and working standard.

12.3 Use the check standard to determine if each element is in calibration. When the results obtained with the check

standard are within 5 % (relative) of the expected concentrations for all elements, proceed with the analysis. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration.

12.4 Calibration curves can be constructed differently, depending on the implementation of internal standard compensation.

12.4.1 When analyte intensities are ratioed to internal standard intensities, the calibration curve is, in effect, a plot of $I(Re)$ versus analyte concentration and:

$$I(Re) = (I(e) - I(Be)) / I(is) \qquad (1)$$

where:
$I(Re)$ = intensity ratio for analyte e,
$I(e)$ = intensity for analyte e,
$I(Be)$ = intensity of the blank for analyte e, and
$I(is)$ = intensity of internal standard element.

12.4.2 When internal standard compensation is handled by multiplying all results for a certain test specimen by the ratio of the actual internal standard concentration to the determined internal standard concentration, the calibration curve is, in effect, a plot of $(I(e) - I(Be))$ versus analyte concentration.

13. Analysis

13.1 Analyze the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points (required), plasma conditions, and so forth). Between test specimens nebulize dilution solvent for a minimum of 60 s.

13.2 When the concentration of any analyte exceeds the linear range of the calibration, prepare another test specimen by mixing the sample with base oil before adding diluent (refer to 11.2.1, for example). Then, reanalyze.

13.3 Analyze the check standard after every fifth test specimen solution. If any result is not within 5 % of the expected concentration, recalibrate the instrument and reanalyze the test specimen solutions back to the previous acceptable check standard analysis.

14. Quality Assurance/Quality Control (QA/QC) (Required)

14.1 Confirm the performance of the instrument and the test procedure by analyzing a QC sample. See Guide D6792 for guidance.

14.1.1 When QA/QC protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

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

14.2 Users of this test method are advised that in contractual agreements, one or more of the contracting parties can and may make Appendix X1 a mandatory practice.

TABLE 1 Precision of Phosphorus Determination

Repeatability	$0.00317\ X^{1.32}$
Reproducibility	$0.01115\ X^{1.32}$
where X = the mean concentration of phosphorus, mg/kg	

TABLE 2 Calculated Precision, mg/kg, at Selected Phosphorus Concentrations, mg/kg

Phosphorus, mg/kg	Repeatability, mg/kg	Reproducibility, mg/kg
500	11.6	40.7
600	14.7	51.8
700	18.1	63.5
800	21.5	75.8

15. Calculation and Report

15.1 Calculate concentrations, based on sample, using Eq 1. Generally, the ICP software performs this calculation automatically.

$$C = S \times [W1 + W2 + W3] / W1 \qquad (2)$$

where:
C = analyte concentration in the sample, mg/kg,
S = analyte concentration in the test specimen, mg/kg (refer to Section 13),
$W1$ = sample mass, g,
$W2$ = diluent mass, g, and
$W3$ = base oil mass (if any), g.

15.2 For each analyte, report mg/kg to three significant figures.

16. Precision and Bias [6]

16.1 *Precision*—The precision of this test method was determined by statistical analysis of interlaboratory results. Ten participating laboratories analyzed nine samples in duplicate. In this study, dilution solvents were limited to mixed xylenes, o-xylene, and kerosine. All laboratories used a peristaltic pump, and internal standard and background correction. The phosphorus content of the samples used in this study was in the concentration range 500 to 800 mg/kg.

16.1.1 *Repeatability*—The difference between 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 the test method, exceed the values in Table 1 only in one case in twenty. (Also, see Table 2.)

16.1.2 *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 the test method, exceed the values in Table 1 only in one case in twenty. (Also, see Table 2.)

16.2 *Bias*—Since there are no NIST standard reference materials of GF 4 type oils with certified phosphorus content available, the bias of the test method could not be determined.

17. Keywords

17.1 additive-elements; emission-spectrometry; GF 4 oils; ICP-AES; inductively-coupled plasma atomic emission spectrometry; internal standard; lubricating oils; phosphorus

APPENDIXES

(Nonmandatory Information)

X1. GENERIC QUALITY CONTROL STATEMENT FOR D02 TEST METHODS

X1.1   Confirm the performance of the instrument or the test procedure by analyzing a QC sample that is, if possible, representative of the samples typically analyzed.

X1.2   Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL7[7]).

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 test process (see Practice D6299, Guide D6792, and MNL7[7]). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4   In the absence of explicit requirements given in the

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[7] *ASTM MNL 7, Manual on Presentation of Data Control Chart Analysis*, Section 3, "Control Chart for Individuals," 6th ed., ASTM International.

test method, 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 is routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the ASTM test method precision to ensure data quality.

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

X1.6   Refer to relevant documents (see Practice D6299, Guide D6792, and MNL7[7]) for further guidance on QC and control charting techniques.

X2. AIDS TO THE ANALYST

X2.1   Check the temperature control of the ICP and ensure stable environmental conditions. This can include temperature control of the spray chamber.

X2.2   Employ adequate mixing and sampling procedures. Ultrasonic homogenizers and vortex mixers are recommended.

X2.3   Use the analytical wavelengths and background correction option specified in the test method. When there is a choice of analytical wavelengths, choose sensitive lines. Ensure that the selected lines are not subject to spectral interferences.

X2.4   When spectral interferences cannot be avoided, determine and implement accurate interference correction factors.

X2.5   When preparing multi-element standards, ensure that the various reagents are mutually soluble.

X2.6   Before use, check the accuracy of element concentrations of commercially-obtained standards. Either compare with alternative sources or analyze by independent methods.

X2.7   Ensure that the samples and standards are not contaminated by glassware or any other piece of apparatus that could affect the results.

X2.8   Select solvents and other reagents that do not contain significant levels of the analytes. Wavelength scanning can indicate contaminated reagents.

X2.9   By experiment, determine the frequency of standards preparation. Then, prepare fresh, as needed.

X2.10   Periodically, as needed, determine the linearity of the calibration curves. Perform quantitative analyses with linear curves only.

X2.11   Inspect the torch for cracks. Discard defective torches.

X2.12   Use clean torches that do not have carbon accumulation.

X2.13   After initially igniting the plasma, allow the instrument to warm up a minimum of 30 min.

X2.14   Inspect the peristaltic pump tubing daily, and replace deteriorating tubing. Daily replacement is recommended.

X2.15   Prepare and analyze reagent blanks. When blank values are significant, correct for the blank or select alternative reagents that give insignificant blank values.

X2.16   To minimize memory effects, allow sufficient solvent rinse time (minimally, 60 s) between determinations.

X2.17 Report results using the number of significant figures specified in the test method.

X2.18 Dilute the standard oils and sample oils by the same factor. This factor should be in the range specified by the test method.

X2.19 Implement internal standardization as specified by the test method.

X2.20 When carbon buildup in the torch is problematic, adjust the experimental conditions to eliminate the problem. Such adjustments can include (1) reducing the sample uptake rate, (2) increasing the intermediate argon gas flow rate, (3) using a jacketed, chilled spray chamber, and (4) lowering the torch, relative to the RF load coil.