Designation: D4047 – 13

Designation: 149/93

Standard Test Method for Phosphorus in Lubricating Oils and Additives by Quinoline Phosphomolybdate Method[1]

This standard is issued under the fixed designation D4047; 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 determination of 0.005 to 10.0 mass % phosphorus in unused lubricating oil and additive concentrates. There is no reason to doubt its applicability to filtered, used lubricating oils, but no systematic study of this application has been made.

1.2 The test method is applicable to samples containing any of the phosphorus compounds in normal use.

NOTE 1—This test method extends the scope of the previous version of IP 149 and replaces IP 148 and the previous version of IP 149 as a referee method.

1.3 This test method is free from most interferences because the high insolubility of the quinoline phosphomolybdate precipitate leads to constant composition and freedom from most adsorbed or occluded impurities, especially from cations which would otherwise interfere in the subsequent titration of the precipitate.

1.4 Barium, calcium, magnesium, zinc, iron, aluminum, alkali salts, citric acid and citrates, chromium up to 18 times the phosphorus content, and titanium up to 3.5 times do not interfere with the test method.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.* For specific hazard statements, see 6.9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

2.2 *IP Standard:*

IP 148 Test Method for Phosphorous in Lubricating Oils and Additives[3]

3. Summary of Test Method

3.1 Additive concentrates are diluted with phosphorus-free white oil to produce a working blend.

3.2 The sample is ignited with excess of zinc oxide whereby phosphorus is converted to phosphate. The residue is dissolved in hydrochloric acid and any sulfide formed is oxidized with potassium bromate. Phosphorus is then precipitated as quinoline phosphomolybdate and determined volumetrically by addition of excess standard alkali and back titration with standard acid.

4. Significance and Use

4.1 Knowledge of the phosphorus content, and thus the phosphorus-containing additives, in a lubricating oil or additive can be used to predict performance characteristics.

5. Apparatus

5.1 *Silica Crucibles,* 40-mm internal diameter at the top and 40 mm in height. The internal surface should be smooth and free from pitting.

5.2 *Muffle Furnace,* capable of maintaining a temperature of approximately 700°C, and fitted with ports to allow air circulation.

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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.

Current edition approved June 15, 2013. Published August 2013. Originally approved in 1981. Last previous edition approved in 2011 as D4047–00 (2011). DOI: 10.1520/D4047-13.

[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.

[3] Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

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

5.3 *Beakers,* 25-mL capacity.

5.4 *Filtering Apparatus,* a filter flask of capacity 500 mL, provided with a glass crucible adapter fitted in a rubber bung together with a rubber sleeve.

5.5 *Gooch Crucible,* porcelain, 35 mm diameter at the top, or a filter funnel fitted with a porcelain filter disk of approximately 20 mm diameter.

5.6 *Filter Pad,* approximately 20 mm diameter.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II or Type III of Specification D1193.

6.3 *Hydrochloric Acid,* approximately 1 *N* reagent solution.

6.4 *Hydrochloric Acid* (36 mass %)—Concentrated hydrochloric acid (HCl).

6.5 *Hydrochloride Acid,* (0.1 *N)*—Hydrochloric acid (HCl) accurately standardized.

6.6 *Mixed Indicator*—Mix 2 volumes of phenolphthalein solution with 3 volumes of thymol blue solution.

6.7 *Phenolphthalein Solution,* (1 g/L in 95 % volume ethanol).

6.8 *Potassium Bromate* ($KBrO_3$), solid.

6.9 *Quinoline* (**Warning—**Quinoline has a high toxic acute systemic rating.)—Redistilled synthetic or, if this is unobtainable, quinoline freshly distilled from the technical product. Collect the colorless distillate in the boiling range from 232 to 238°C. Store the quinoline in an amber bottle in the dark.

6.10 *Quinoline Hydrochloride Solution*—Dissolve 20 mL of quinoline in 800 mL of hot water acidified with 25 mL of concentrated HCl; add a little paper pulp, cool, filter, and make up to 1 L with water. This solution is stable for about 1 month.

6.11 *Sodium Hydroxide Solution* (0.1 *M)*—Sodium hydroxide (NaOH) accurately standardized.

6.12 *Sodium Molybdate Solution*—Dissolve 10 g of sodium hydroxide (NaOH) and 18 g of ammonia-free molybdenum trioxide in 200 mL of water and filter the solution.

NOTE 2—To avoid high blanks caused by silicate interference with alkaline reagents, including sodium molybdate solution, store in polythene containers.

6.13 *Thymol Blue Solution* (1 g/L) in 95 % volume ethanol.

6.14 *Zinc Oxide* (ZnO), finely divided.

6.15 *Lead Acetate Test Paper.*

6.16 *Fluorescein Test Paper*—Prepare by dipping a strip of filter paper into a 1 g/L solution of fluorescein, sodium salt, in 95 vol % ethanol.

6.17 *White Oil,* containing less than 0.005 mass % phosphorus.

7. Blending Procedure

7.1 Samples having a phosphorus content greater than 0.3 mass % should be blended in white oil to give a phosphorus content in the range of 0.1 to 0.3 mass %.

7.2 Calculate the mass of sample for a 10-g blend as follows:

$$A = 2/P \qquad (1)$$

where:

P = approximate percent phosphorus in the sample, and
A = grams of sample required for a 10-g blend.

7.3 Calculate the mass of white oil for a 10-g blend as follows:

$$B = 10 - A \qquad (2)$$

where:

B = mass of white oil, g.

7.4 Weigh a quantity of sample $A \pm$ 0.01 g into a 25-mL beaker.

7.5 Weigh into the same beaker B g of white oil.

7.6 Mix the sample and white oil thoroughly by stirring and warming to approximately 50°C.

8. Procedure

8.1 For additive concentrates, weigh into a crucible 1 g of the homogenized blend prepared in 7.6.

8.2 For lubricating oils, weigh into a crucible 3 g of sample or smaller amount estimated to contain not more than 3 g of phosphorus. The amount of sample to be taken is indicated in Table 1.

TABLE 1 Amount of Sample

Phosphorus Content, mass %	Approximate Mass of Sample, g	Approximate Volume of 0.1 M NaOH solution required	
		P%m	mL
0.005 to 0.10	3	0.005	1.3
		0.010	2.5
		0.05	13
		0.10	25
Above 0.10 to 0.30		0.10	8
		0.20	17
		0.30	25

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[4] *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 *Analar 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.

8.3 Cover the sample with 8 g of zinc oxide and level the surface. Apply heat from a Meker burner to the surface until the zinc oxide becomes red hot; then gently heat the crucible from below with a small bunsen flame so that the oil burns off very gently. Finally, when no more vapor is evolved, ignite strongly and transfer to a muffle furnace at 700°C to burn off residual carbon.

8.4 Allow the crucible to cool and carefully transfer its contents to a 600-mL beaker (Note 3), completing the transfer with a jet of water from a wash bottle. Add about 50 mL of water to the contents of the beaker and rinse the crucible with a few millilitres of concentrated HCl. Add the acid rinsing to the beaker and then sufficient concentrated HCl to bring the total volume of acid added to 23 mL.

8.5 Heat the contents of the beaker until all the ZnO is dissolved, then boil until all hydrogen sulfide has been expelled from the solution (test with lead acetate paper). Allow to cool slightly, add 30 to 50 mg of $KBrO_3$, and boil until all free bromine has been expelled from the solution (test with fluorescein paper).

NOTE 3—Glass apparatus should have good resistance to alkali. Do not use scratched or etched beakers for the precipitation of quinoline phosphomolybdate.

8.6 Dilute the liquid to a volume of about 150 mL with water, add 30 mL of concentrated HCl and 30 mL of sodium molybdate solution, rinsing the sides of the beaker with a little water after each addition. Place the beaker on the hot plate and bring the liquid to the boil. Add a few drops of quinoline hydrochloride reagent from a coarse-tipped buret or pipet, swirling during the addition.

8.7 Bring to the boil again and add 2 mL of the reagent dropwise with swirling. To the gently boiling liquid add the reagent in 2-mL increments until a total of 24 mL has been added, swirling during the addition. Stand the beaker on the edge of the hot plate or on a boiling water bath for 15 min for the precipitate to settle. Cool to room temperature.

8.8 Prepare a paper pulp pad (Note 4) in a funnel fitted with a porcelain filter disk and tamp down well. Decant the clear supernatant liquid through the filter with applied suction and wash the precipitate twice by decantation with 20-mL portions of 1 *M* HCl. Transfer the precipitate to the filter pad with cold water and wash the beaker several times with volumes of 25 to 30 mL of water to free the beaker from acid. Use these washes also to wash the precipitate on the filter, allowing each portion of liquid to pass through before pouring on the next. Continue to wash until one portion of wash liquid fails to decolorize the solution when passed into a clean flask containing a few drops of phenolphthalein solution and 1 drop of 0.1 *N* NaOH solution. Six washes are usually sufficient.

NOTE 4—This can be made conveniently by placing an intact 20-mm diameter accelerator disk in the funnel, moistening, and applying gentle suction.

8.9 Transfer the precipitate, pad, and disk to the 500-mL conical flask. This can be done conveniently with a glass rod having a drawn-out pointed end. Insert the funnel in the flask and wash into it any portions of the precipitate remaining in the funnel, using CO_2-free water. Remove any traces of precipitate adhering to the funnel by wiping with a slip of moist filter-paper; add this to the contents of the flask. Add CO_2-free water until the volume of liquid in the flask is about 120 mL.

8.10 Shake the flask until the pulp pad is disintegrated and the precipitate is thoroughly dispersed. Ensure that no lumps remain otherwise difficulty may be encountered in dissolving them in the NaOH solution.

8.11 From a buret slowly add 0.1 *M* NaOH solution shaking the flask vigorously to ensure complete solution of the precipitate. Continue to add 0.1 *M* NaOH solution until the precipitate has dissolved and add approximately 5 mL in excess. Use Table 1 to estimate the volume of alkali required. Record the volume of 0.1 *M* NaOH solution added (V_1). Add about six drops of mixed indicator and titrate with 0.1 *M* HCl until the color changes from violet through gray and suddenly to pale yellow. Record the volume of 0.1 *M* HCl used (V_2).

8.12 Make a blank determination omitting the sample. In the final titration add 5.0 mL of 0.1 *M* NaOH solution and titrate with 0.1 *M* HCl (V_3).

9. Calculation

9.1 *Blended Samples*—Calculate the phosphorus content of blended samples as follows:

$$\text{Phosphorus, mass \%} = \frac{\left[(V_1 - V_2) - (5 - V_3)\right] \times 0.01191 \times (A + B)}{W \times A} \quad (3)$$

where:

A = mass of original sample in 10 g blend, g
B = mass of white oil in 10-g blend, g,
W = mass of blend taken for determination, g,
V_1 = volume of 0.1 *M* NaOH solution added, mL,
V_2 = back titration with 0.1 *M* HCl, mL,
V_3 = back titration, for blank, with 0.1 *M* HCl, mL.

9.2 *Unblended Samples*—Calculate the phosphorus content of unblended samples from the following equation:

$$\text{Phosphorus, mass \%} = \frac{\left[(V_1 - V_2) - (5 - V_3)\right] \times 0.01191}{W} \quad (4)$$

where:

W = weight of sample taken, g,
V_1 = volume of 0.1 *M* NaOH solution added, mL,
V_2 = back titration with 0.1 *M* HCl, mL, and
V_3 = back titration, for blank, with 0.1 *M* HCl, mL.

10. Report

10.1 Report result to three significant figures as the Phosphorus Content, Test Method D4047 and IP 148.

11. Quality Control

11.1 Confirm the performance of the test procedure by analyzing a quality control sample which is stable and representative of the sample of interest.

11.1.1 When the quality control/quality assurance protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

11.1.2 When there is no quality control/quality assurance protocol established in the testing facility, Appendix X1 can be used to perform this function.

12. Precision and Bias

12.1 The precision of this method as obtained by statistical examination of interlaboratory results[5] is as follows:

12.1.1 *Repeatability*—The difference between successive 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 following values in only one case in twenty, where x = average of the two test results.

Level of result (x)	0.005 – 0.079%	0.08 – 10%
Repeatability	0.032 (x + 0.04)	$0.0318x^{0.992}$

12.1.2 *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 following values in only one case in twenty, where x = average of the two test results.

Level of result (x)	0.005 – 0.079%	0.08 – 10%
Reproducibility	0.074 (x + 0.04)	$0.118x^{0.992}$

12.2 Precision is given in Table 2 for typical values of x. These precision values have been obtained by statistical examination of interlaboratory results and are published for the first time in 1979.

12.3 *Bias*—The bias of this test method cannot be determined since an appropriate standard reference material containing a known level of phosphorus in liquid petroleum hydrocarbon is not available.

13. Keywords

13.1 additives; lubricating oils; phosphomolybdate; phosphorous

TABLE 2 Repeatability and Reproducibility

Phosphorus x	Repeatability	Reproducibility
0.007	0.001	0.003
0.01	0.001	0.003
0.02	0.002	0.004
0.04	0.002	0.006
0.07	0.003	0.008
0.1	0.003	0.012
0.2	0.006	0.024
0.4	0.013	0.047
0.7	0.022	0.083
1.0	0.032	0.118
2.0	0.063	0.234
4.0	0.126	0.467
7.0	0.219	0.813
10.0	0.312	1.153

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

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 and *ASTM MNL 7*).[6]

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 and *ASTM MNL 7*).

X1.4 In the absence of explicit requirements given in the 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 is 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 precision should be checked against the ASTM 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 material routinely analyzed. An ample supply of QC sample material

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[5] A research report is not available.

[6] *ASTM MNL 7*, “Manual on Presentation of Data Control Chart Analysis,” 6th ed., available from ASTM Headquarters.

should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X1.6 See Practice D6299 and *ASTM MNL 7* for further guidance on QC and Control Charting techniques.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D4047 – 00 (2011)) that may impact the use of this standard.

(1) Added information in new sections 1.3, 1.4, 5.4, 5.5, 5.6, 6.15, 6.16, and 6.17 in Scope, Apparatus, and Reagents and Materials sections to keep consistent with its counterpart IP 149 test method.

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