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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 U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of ~~0.005~~0.005 % to ~~10.0~~ 10.0 % by 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 6.9.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum ~~Products~~ Products, Liquid Fuels, 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.

[3] Available from Energy Institute, 61 New Cavendish St., London, ~~WIG~~W1G 7AR, U.K., ~~http://www.energyinst.org.uk.~~http://www.energyinst.org.

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

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~~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,~~700 °C, and fitted with ports to allow air circulation.

5.3 *Beakers,* ~~25-mL~~25 mL capacity.

5.4 *Filtering Apparatus,* a filter flask of capacity ~~500 mL,~~ 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~~ 20 mm diameter.

5.6 *Filter Pad,* approximately ~~20 mm~~ 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 %)~~(36 % by 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~~(1 g ~~g/L in 95 % /~~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~~232 °C to ~~238°C.~~238 °C. Store the quinoline in an amber bottle in the dark.

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

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

6.12 *Sodium Molybdate Solution*—Dissolve ~~10 g~~ 10 g of sodium hydroxide (NaOH) and ~~18 g~~ 18 g of ammonia-free molybdenum trioxide in ~~200 mL~~ 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~~(1 g ~~g/L) in 95 % /~~L) in 95 % volume ethanol.

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

6.15 *Lead Acetate Test Paper.*

[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.

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

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

7. Blending Procedure

7.1 Take samples in accordance with the instructions in Practices D4057 or D4177.

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

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

$$A = 2/P \tag{1}$$

~~*where:*~~
where:

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

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

$$B = 10 - A \tag{2}$$

~~*where:*~~
where:

B = mass of white oil, g.

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

7.6 Weigh into the same beaker B ~~g~~ g of white oil.

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

8. Procedure

8.1 For additive concentrates, weigh into a crucible ~~1 g~~ 1 g of the homogenized blend prepared in ~~7.6~~7.7.

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

8.3 Cover the sample with ~~8 g~~ 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~~700 °C to burn off residual carbon.

8.4 Allow the crucible to cool and carefully transfer its contents to a ~~600-mL~~600 mL beaker (Note 3), completing the transfer with a jet of water from a wash bottle. Add about ~~50 mL~~ 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.~~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~~30 mg to ~~50 mg~~ 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.

TABLE 1 Amount of Sample

Phosphorus Content, ~~mass %~~ % by 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