Designation: D1091 – 00 (Reapproved 2005)

Standard Test Methods for Phosphorus in Lubricating Oils and Additives[1]

This standard is issued under the fixed designation D1091; 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 These test methods cover the determination of phosphorus in unused lubricating oils and lubricating oil additives and their concentrates. The test methods are not restricted with respect to the type of phosphorus compounds that may be present—for example, trivalent or pentavalent phosphorus compounds, phosphines, phosphates, phosphonates, phosphorus sulfides, and so forth—since all are quantitatively converted to an aqueous solution of orthophosphate ion by oxidation of the sample during the course of analysis.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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]

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

3. Summary of Test Method

3.1 Organic material in the sample is removed and the phosphorus is converted to phosphate ion by oxidation with sulfuric acid, nitric acid, and hydrogen peroxide. One of two procedures is then followed:

	Sections
Photometric (Molydivanado) Method	7-18
Gravimetric Method	7-11 and 19-25

3.2 The photometric method is used where the phosphorus content is estimated to be under 2 %, and the gravimetric method is used for phosphorus contents of 2 % or over.

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. This test method is suitable for most applications requiring the determination of phosphorus.

5. Purity of Reagents

5.1 *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.[3] 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.

5.2 *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. Sampling

6.1 Obtain samples in accordance with the instructions in Practices D4057 or D4177.

6.2 Take care that the test specimen is thoroughly representative of the material to be tested and that the portion of the sample is thoroughly representative of the test unit.

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[1] These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the responsibility of Subcommittee D02.03 on Elemental Analysis.

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This test method has been adopted for use by government agencies to replace Method 5661 of Federal Test Method Standard No. 791b DOI: 10.1520/D1091-00R05.

[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] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, D.C. 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.

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

TABLE 1 Sample Size

Phosphorus Content, %	Approximate Weight of Sample, g	Precision of Weighing, plus or minus, g
Photometric (Molybdivanado) Method		
0.002 to 0.2	2	0.004
0.2 to 2	0.2	0.0004
Gravimetric Method		
2 to 5	2	0.004
5 to 10	1	0.003
10 to 15	0.7	0.002
15 to 25	0.4	0.001

OXIDATION OF THE SAMPLE

7. Scope

7.1 This test method covers a procedure for removal of organic material and subsequent conversion of phosphorus to phosphate ion in samples of unused lubricating oils, lubricating oil additives, and their concentrates.

8. Summary of Test Method

8.1 Organic material in the sample is destroyed and the phosphorus is converted to phosphate ion by oxidation with sulfuric acid, nitric acid, and hydrogen peroxide. The residual hydrogen peroxide is removed by diluting with water and evaporating several times to dense white fumes.

9. Apparatus

9.1 *Digestion Flasks*, Kjeldahl flasks, 300 mL, ground-glass stoppered.

9.2 *Digestion Rack*—A digestion rack constructed to hold one or more 300-mL Kjeldahl flasks at an angle of approximately 45° in such a fashion that direct heat is applied only to the bottom of the flask and such that the body and neck of the flask are insulated from the source of heat. Approximately three-fourths of the neck of the flask should be cooled by air at atmospheric temperature, preferably by directing an air stream against the neck of the flask. A Bunsen flame or high capacity electric heater are suitable heat sources.

10. Reagents

10.1 *Hydrogen Peroxide (30 %)*, concentrated hydrogen peroxide (H_2O_2) (**Warning**—Concentrated solutions are highly toxic and strong oxidants.) containing no more than 0.0002 % phosphorus.

10.2 *Nitric Acid (sp gr 1.42)*, concentrated nitric acid (HNO_3).

10.3 *Sulfuric Acid (sp gr 1.84)*, concentrated sulfuric acid (H_2SO_4).

10.4 *White Oil*, phosphorus-free.

10.5 *Quality Control (QC) Samples*, preferably, portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process, as described in Section 26.

11. Procedure

11.1 Weigh out a portion of the material to be analyzed, in accordance with Table 1, into a 300-mL Kjeldahl flask. Any convenient method of transferring the test specimen may be used as long as care is taken to avoid getting the test specimen on the neck of the flask (see Note 1). Add H_2SO_4 (3 mL for the photometric procedure, or 10 mL for the gravimetric procedure) and a 6-mm glass bead (see Note 2), and swirl the flask to mix the contents.

11.2 To obtain satisfactory accuracy with the small amounts of phosphorus involved, it is necessary to take extensive precautions in handling. The usual precautions of cleanliness, careful manipulation, and avoidance of contamination should be scrupulously observed; also, all glassware should be cleaned before use, with cleaning acid or by some procedure that does not involve use of commercial detergents. These compounds often contain alkali phosphates, which are strongly absorbed by glass surfaces and are not removed by ordinary rinsing. It is desirable to segregate a special stock of glassware for use only in the determination of phosphorus.

NOTE 1—The volume occupied by the glass bead (0.1 mL) can be ignored for ordinary work. Excessive bumping is encountered occasionally in the digestion of some organic phosphorus compounds. This bumping can be minimized by using a glass bead. Some difficulty can be experienced when using commercial boiling aids in obtaining a solution clear enough for photometric measurement of phosphorus (see Sections 12-18) even after centrifuging, due to the attrition of these boiling aids under the vigorous digestion procedure.

11.3 Make a blank determination following the same procedure and using the same amounts of all reagents and a similar size sample of phosphorus-free white oil. This blank is for use in the photometric method (see Sections 12-18).

11.4 Place the flask on the digestion rack under a hood and warm gently with a micro burner until the test specimen is charred, while cooling the neck of the flask, preferably by use of an air stream (see Note 2). Continue heating until dense white fumes appear (see Note 3). While boiling, continuously add 1 mL of HNO_3 dropwise (see Note 4) to oxidize the organic material. When the HNO_3 has boiled off and dense white fumes reappear, repeat the treatment with an additional 1 mL of HNO_3 (see Note 5). Continue the addition of HNO_3 in 1-mL increments until the digestion mixture is no darker than a straw color, indicating that almost all the organic matter has been oxidized.

NOTE 2—The amount of air used to cool the neck of the flask will at times have to be reduced or even shut off to allow vapors and fumes to leave the flask and to allow sample to come to dense white fumes. However, this should not be done until the test specimen is in a well-decomposed state; the air stream should be turned on again each time before the addition of the HNO_3 or H_2O_2 (see 11.4).

NOTE 3—Excessive evaporation of H_2SO_4 should be avoided to minimize any loss of phosphorus that may occur. Care should be exercised to avoid heating above the liquid level. Since there is some indication that with test specimens containing inorganic compounds (that is, barium or lead salts) there can be losses of phosphorus due to sintering or fusion of the phosphate and sulfate to the glass, it is well to examine the dried vessel after use to detect any opaque film of fused material.

NOTE 4—Unless the HNO_3 is added dropwise, it can force excessive amounts of vapor from the flask and lead to loss of phosphorus containing fumes.

NOTE 5—To minimize the loss of H_2SO_4 in the digestion process, it is advisable not to prolong the dense white fumes stage between addition of HNO_3.

11.5 Cool the flask slightly and add 10 drops (0.5 mL) of H_2O_2. Heat until dense white fumes appear, and while boiling, cautiously add 1 mL of HNO_3 dropwise. When the HNO_3 has boiled off and dense white fumes reappear, repeat the treatment with H_2O_2 and HNO_3 until the digestion mixture is colorless, at which time the organic material will be completely oxidized. Four treatments will usually suffice. The total amount of H_2O_2 used should be noted, and the same amount used for each test specimen and the blank.

11.6 When oxidation is complete, allow the flask to cool, wash down the mouth and neck with a minimum amount of water (5 mL), and mix the contents. Return the flask to the digestion rack and continue heating to the appearance of dense white fumes. Repeat the process of the addition of water and heating to dense fumes several times. This will remove all traces of H_2O_2. (**Warning**—Use extreme care in fuming, in accordance with 11.5, to remove all traces of H_2O_2 so that no color interference will be experienced when phosphorus is to be determined photometrically, as described in Sections 12-18.)

PHOTOMETRIC (MOLYBDIVANADO) METHOD

12. Scope

12.1 This test method covers determination of total phosphorus in concentrations of less than two mass % (see Note 6), calculated on the basis of the original test specimen, in samples treated by the acid-oxidation procedure described in Sections 7-11.

NOTE 6—For phosphorus concentrations greater than or equal to two mass %, see Sections 19-25.

13. Summary of Test Method

13.1 After oxidation of organic material in the test specimen and quantitative conversion of the phosphorus to phosphate ion, the acidity of the digestion mixture is adjusted and the mixture diluted to suitable volume. Solutions of ammonium vanadate and ammonium molybdate are added in the order named. The addition of the molybdate solution to the acid vanadate-phosphate mixture results in the formation of a heteropoly acid, molybdivanadophosphoric acid, which is yellow in color. Although the exact composition of molybdivanadophosphoric acid is uncertain, solutions of this compound, when formed in accordance with carefully prescribed conditions, have been found to conform to the Beer-Lambert law for optical transmittance measurements made at 420 to 470 nm as a function of phosphorus content.

14. Apparatus

14.1 *Photoelectric Photometer*—A spectrophotometer capable of isolating a 5-nm spectral band at 430 and 460 nm is a suitable instrument for use in this determination. The instrument should be equipped with auxiliary facilities for handling 1, 2, and 5-cm cells, and a supply of these should be available. Other instruments such as photoelectric filter photometers may also be used.

NOTE 7—While not as desirable as photometers, visual color comparators can also be used, if necessary.

15. Reagents

15.1 *Ammonium Molybdate Solution*—Dissolve 50 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in warm water and dilute to 1 L. Filter before using.

15.2 *Ammonium Vanadate Solution*—Dissolve 2.5 g of ammonium vanadate (NH_4VO_3) in 500 mL of hot water, add 20 mL of concentrated nitric acid (HNO_3 relative density 1.42), and dilute to 1 L.

15.3 *Phosphate, Standard Solution (1 mL = 0.1 mg P)*—Dissolve 0.4393 g of potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 L. For best work, the salt should be twice recrystallized and vacuum-dried before use.

15.4 *Sulfuric Acid (relative density 1.84)*, concentrated sulfuric acid (H_2SO_4).

15.5 *QC Samples*, preferably, portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process, as described in Section 26.

16. Calibration and Standardization

16.1 Introduce 0, 0.4, 0.8, 1.6, 2.4, 4.0, 4.8, 8.0, 16, 24, and 32 mL of standard phosphate solution into 100-mL ground-glass-stoppered volumetric flasks. Add sufficient H_2SO_4 of any convenient concentration such that the final acid concentration after dilution to 100 mL will be 0.5 N. Dilute to 55 to 60 mL, and add 10 mL of ammonium vanadate solution and ammonium molybdate solution, in the order named, with adequate mixing between additions. Dilute to 100 mL, close with a ground-glass stopper, and mix thoroughly. Allow to stand at least 45 min but no longer than 60 min to develop the color.

16.2 Using the 1-cm cell and with the wave length set at 460 nm, adjust the photometer to read 100.0 % transmittance with the zero phosphate (reagent blank) standard. Although absorption cells are usually very closely matched, for best work it is recommended that two cells be used and that one be reserved for the blank and the other for the standard or sample solutions. Obtain transmittance measurements on solutions containing 0.4, 0.8, 1.6, 2.4, and 3.2 mg of phosphorus. These standards should give measurements falling between 90 and 20 % respectively. After making a measurement, return to the reagent blank cell. This should check the 100.0 % setting within 0.2 %. Repeat the reading of the standard and return to the blank. Obtain three readings in all of each standard solution. Using semilog graph paper, plot the average transmittance as a function of phosphorus content. The resultant curve should be a straight line.

16.3 In a similar manner, prepare calibration curves at 460 nm for the 2 and 5-cm cells, selecting concentrations from the series of standards that give readings between 20 and 90 %.

16.4 Finally, prepare a calibration curve for the 5-cm cell, using a wavelength setting of 430 nm. At this wavelength the molybdivanadophosphoric acid has a higher optical density, and the curve obtained will have a steeper slope. The advantages of having this calibration at the second wavelength are two-fold: (1) it provides increased sensitivity in the region of low concentrations, and (2) it provides an independent confirmation of measurements made at 460 nm. Agreement between measurements at both wavelengths is a criterion of the absence of interference.

17. Procedure

17.1 To the cooled, decomposed sample in the Kjeldahl flask (see 11.5), add by visual observation sufficient H_2SO_4 to bring the acidity to approximately one half the concentration present at the beginning of the acid-oxidation procedure (see 11.1). This step may not always be necessary (see Note 8). Cool the flask and contents and transfer to a 100-mL volumetric flask, using approximately 50 mL of water. (**Warning**—Extreme care should be exercised when adding water to H_2SO_4. It is advisable to add the water slowly, a small amount at a time, allowing it to run down the side of the flask, which is adequately cooled.)

NOTE 8—The acidity of the solution after acid oxidation is critical, since interference occurs from the appearance of an orange-yellow color, which forms in a neutral or too acid solution. The acidity for proper development of the desired color should be in the range from 0.4 *N* to 0.6 *N* in H_2SO_4. Adjustment of acidity can not be required when the losses of H_2SO_4 have been kept to a minimum in the fuming steps of the acid-oxidation procedure; however, it may be necessary to further evaporate H_2SO_4 in order to bring the acidity of the solution to approximately optimum normality.

17.2 Add 10 mL each of ammonium vanadate solution (see Note 9) and ammonium molybdate solution. It is important that these solutions be added in the order named, with adequate mixing between additions, to ensure the reproducible composition of the complex. Dilute to 100 mL, stopper with a ground-glass stopper, and mix thoroughly. Allow to stand at least 45 min but no longer than 60 min to develop the color. Maintain the temperature of this solution within 5°C of the temperature at which the calibration was performed.

NOTE 9—Remove the last trace of hydrogen peroxide since very little hydrogen peroxide is required to develop the maximum color of the vanadium-hydrogen peroxide complex. Any trace of H_2O_2 will be evident by the reddish brown color obtained upon the addition of the vanadium reagent. When such is the case, the sample must be discarded and the acid-oxidation step will have to be repeated on a new test specimen.

17.3 When any insoluble matter is present, transfer a portion of the solution to a centrifuge tube, centrifuge at 1200 rpm for 5 min, and decant the clear supernatant liquid into the absorption cell. If desired, a portion of the solution may be drawn off by means of a filter stick. Avoid the use of filter paper as the colored complex may be adsorbed on it.

17.4 When the approximate phosphorus content is known, the path length of the absorption cell should be chosen to give a transmittance between 25 and 50 %. It is desirable to employ conditions such that readings fall within this range to reduce the error in the photometric measurement. If the phosphorus content is unknown, the analyst, with experience, will be able to select the best cell to use by visual observation. In the case of test specimens that prove to be too highly colored to be read directly, transfer an appropriate aliquot to another volumetric flask and dilute with the reagent blank solution in order to maintain all the reagent concentrations at the proper level. Make all measurements at 460 nm, except for the extremely low concentrations (below 0.25 mg P/100 mL), which shall be made at 430 nm. In making the readings, adjust the galvanometer to 100.0 % with the reagent blank solution in the light path. Insert the sample in the light path, read the percentage transmittance to 0.1 %, and return to the reagent blank, which should check the original setting within 0.2 %. Readjust to 100.0 if necessary and repeat, obtaining at least three readings on the samples. These should agree within 0.2 %. Use the average of these readings to obtain the phosphorus content from the calibration curves.

17.5 *Overall Blank*—Although a reagent blank solution is used in preparing the calibration curves, an overall blank determination should be carried through on a sample of phosphorus-free white oil. No phosphorus should be detectable in such a blank.

18. Calculation

18.1 Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, mass \%} = ((P_s - P_b) \times D \times 100)/(1000 \times S) \quad (1)$$

where:

P_s = milligrams of phosphorus in test specimen read from standard curve,
P_b = milligrams of phosphorus in overall blank read from standard curve,
D = dilution factor, if an aliquot is used (see 17.4), and
S = mass of test specimen.

GRAVIMETRIC METHOD[2]

19. Scope

19.1 This test method covers the determination of total phosphorus in concentrations of 2 mass % or more, (see Note 10), calculated on the basis of the original sample, in samples treated by the acid-oxidation procedure described in Sections 7-11.

NOTE 10—For phosphorus concentrations less than 2 mass %, see Sections 12-18.

20. Summary of Test Method

20.1 After oxidation of organic material in the test specimen and quantitative conversion of the phosphorus to phosphate ion, the phosphate ion is separated from interfering metals by precipitation as ammonium molybdiphosphate in nitric acid solution. After an ammoniacal solution of the phosphate ion is obtained, the phosphorus is precipitated as magnesium ammonium phosphate, ignited, and weighed as magnesium pyrophosphate.

21. Apparatus

21.1 *Electric Muffle Furnace*, capable of operating over a variable temperature range from 200 to 1100°C and of maintaining a temperature of 1050 ± 50°C.

21.2 *Filtering Crucible*, 25-mL porcelain crucibles, having porous bottoms capable of retaining a fine precipitate.[4]

22. Reagents

22.1 *Ammonium Hydroxide (relative density 0.90)*, concentrated ammonium hydroxide (NH_4OH).

22.2 *Ammonium Hydroxide (3+5)*—Mix 3 volumes of NH_4OH (relative density 0.90) with 5 volumes of water.

22.3 *Ammonium Hydroxide (1+24)*—Mix 1 volume of NH_4OH (relative density 0.90) with 24 volumes of water.

22.4 *Ammonium Nitrate*, NH_4NO_3 crystals.

22.5 *Ammonium Nitrate Solution*—Dissolve 50 g of NH_4NO_3 in water and dilute to 1 L.

22.6 *Hydrochloric Acid (relative density 1.19)*, concentrated hydrochloric acid (HCl).

22.7 *Magnesia Mixture*—Dissolve 50 g of magnesium chloride ($MgCl_2·6H_2O$) and 100 g of ammonium chloride (NH_4Cl) in 500 mL of water, add a slight excess of NH_4OH, and allow to stand overnight. Filter, make the solution just acid with HCl, and dilute to 1 L.

22.8 *Methyl Red Indicator Solution (1 g/L)*—Dissolve 0.5 g of methyl red in 300 mL of alcohol (95 % ethyl alcohol or denatured alcohol conforming to Formula No. 3A of the Alcohol, Tobacco, and Firearms Bureau), and dilute with water to 500 mL.

22.9 *Molybdate Reagent*—Dissolve 100 g of ammonium molybdate ($(NH_4)_6·Mo_7O_{24}·4H_2O$) in 400 mL of water. Add 80 mL of NH_4OH (rel dens 0.90) and filter if a precipitate appears. Mix 400 ml of HNO_3(relative density 1.42) with 600 mL of water. Prepare the ammonium molybdate reagent from these solutions immediately before use by slowly mixing 1 volume of the ammonium molybdate solution with 2 volumes of the diluted HNO_3, while stirring rapidly.

22.10 *Nitric Acid (1+1)*—Mix equal volumes of nitric acid (HNO_3, relative density 1.42) and water.

22.11 *QC Samples*, preferably, portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process, as described in Section 26.

23. Procedure for Samples Containing No Metals Other than Alkali Metals

23.1 Cool the Kjeldahl flask (see 11.5), transfer the solution to a 400-mL beaker, and wash the flask with small portions of water until the volume of solution is approximately 100 mL. Boil the solution for 5 to 10 min, cool to near room temperature, and add NH_4OH (rel dens 0.90) until the solution is neutral to methyl red. Make the solution acid with HCl (relative density 1.19), and add 1 mL in excess.

23.2 Add 20 mL of magnesia mixture, slowly and while stirring, and cool the solution to below room temperature in an ice bath. Add NH_4OH (relative density 0.90), slowly and while stirring constantly, until the solution is basic. Continue stirring until most of the precipitate has formed (see Note 11); then add 5 mL of NH_4OH (relative density 0.90) in excess. Allow the precipitate to stand overnight.

23.3 Filter through a weighed porcelain filter crucible of fine porosity, wash with NH_4OH (1+24), and dry in an oven. Place in a cool furnace, gradually raise the temperature to red heat, and ignite at 1050 ± 50°C for 30 to 40 min. Repeat the ignition for similar periods until constant weight is reached.

NOTE 11—For work of highest accuracy, it is generally necessary to test the precipitation technique on known inorganic samples. Reprecipitation sometimes aids in obtaining more accurate values.

24. Procedure for Samples Containing Metals Other than Alkali Metals

24.1 Cool the Kjeldahl flask (see 11.5), add 40 to 50 mL of water, cool to room temperature, and filter the solution through a medium-texture, ashless paper. Collect the filtrate in a 500-mL wide-mouth, glass-stoppered Erlenmeyer flask, and wash the Kjeldahl flask and filter paper thoroughly with water, adding the rinsings to the filtrate; discard the paper. Boil the solution for several minutes, and cool to near room temperature. Add NH_4OH (relative density 0.90) until the solution is neutral to methyl red; then add HNO_3(1+1) until the color just changes to red. Concentrate or dilute the solution to approximately 150 mL.

24.2 Add 15 g of NH_4NO_3 crystals and swirl until dissolved. Adjust the temperature to 35 to 40°C and add 240 mL of freshly prepared molybdate reagent. Stopper the flask, shake vigorously for 4 to 6 min, and allow to stand for at least 2 h, or preferably overnight. Filter the solution through a medium-texture, ashless paper. Wash the precipitate with NH_4NO_3 solution. Do not attempt to transfer all of the precipitate from the flask to the paper; however, reserve the flask for later treatment. Wash the precipitate several times with the wash solution but do not allow the stream of wash solution to strike the funnel above the edge of the paper as the precipitate has a tendency to creep.

24.3 Place a clean 400-mL beaker under the funnel, and dissolve the precipitate through the paper into the beaker with NH_4OH (3+5). Use a little of the NH_4OH to dissolve any of the precipitate that remained in the flask set aside in 24.2 and pour this solution through the paper. Wash the flask, funnel, and paper four times with hot water, once with NH_4OH (3+5), and once again with water. Discard any residue remaining on the paper. Evaporate the solution to a volume of 90 to 100 mL, make the solution acid with HCl, and add 1 mL in excess. Disregard any molybdiphosphate precipitate that may appear at this point.

24.4 Add 20 mL of magnesia mixture, slowly while stirring, and cool the solution to below room temperature in an ice bath. Add NH_4OH (relative density 0.90), slowly and while stirring constantly, until the solution is basic. Continue stirring until most of the precipitate has formed (see Note 10); then add 5 mL of NH_4OH (relative density 0.90) in excess. Allow the precipitate to stand overnight.

24.5 Filter through a weighed porcelain filter crucible (fine porosity), wash with NH_4OH (1+24), and dry in an oven. Place in a cool furnace, gradually raise the temperature to red heat,

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[4] Selas crucible No. 3001 and Gooch crucible have been found satisfactory for this purpose. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.

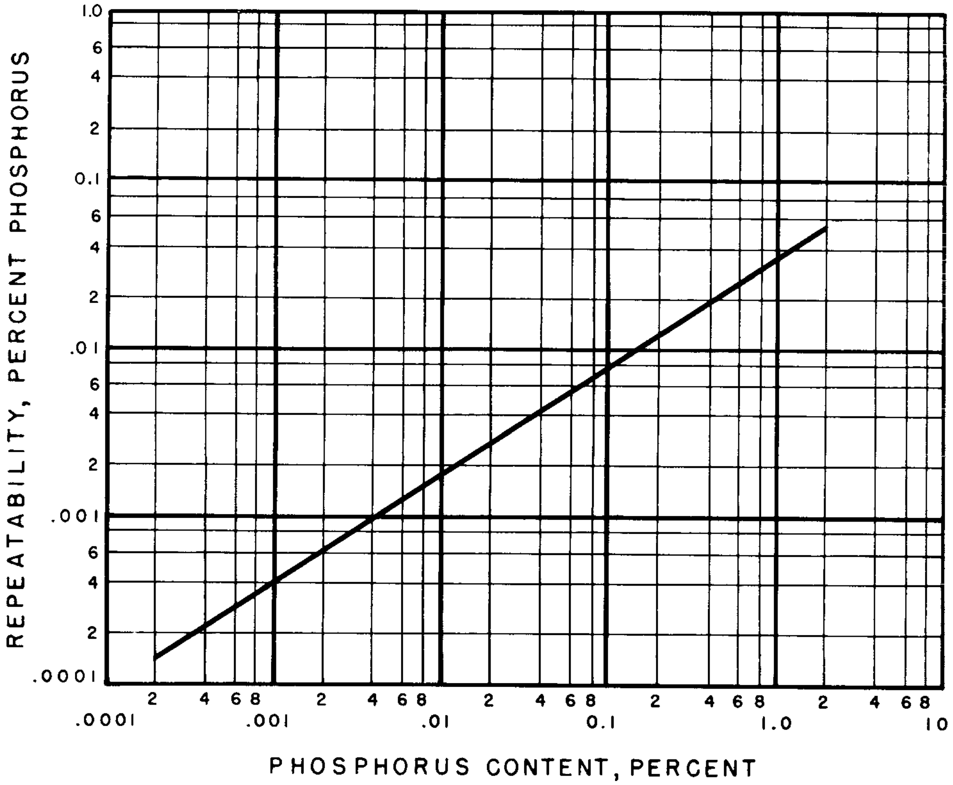

FIG. 1 Repeatability of Test Methods D1091 by Photometric Procedure

and ignite at 1050 ± 50°C for 30 to 40 min. Repeat the ignition for similar periods until constant weight is reached.

25. Calculation

25.1 Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, mass } \% = (P \times 27.84)/W \qquad (2)$$

where:

P = magnesium pyrophosphate, g, and
W = sample used, g.

26. Quality Control (QC)

26.1 Confirm the performance of the instrument of the test procedure by analyzing a QC sample (see 10.5, 15.5, and 22.11).

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

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

27. Precision and Bias [5]

27.1 The precision of these test methods is not known to have been obtained in accordance with currently accepted guidelines.

27.2 The precision of these test methods as obtained by statistical examination of interlaboratory test results is as follows:

27.2.1 *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 only in one case in twenty:

Photometric	Gravimetric
See Fig. 1	Fig. 2

27.2.2 *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 only in one case in twenty:

Photometric	Gravimetric
See Fig. 3	Fig. 4

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

28. Keywords

28.1 additives; gravimetric; lubricating oils; phosphorus; photometric

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1007.

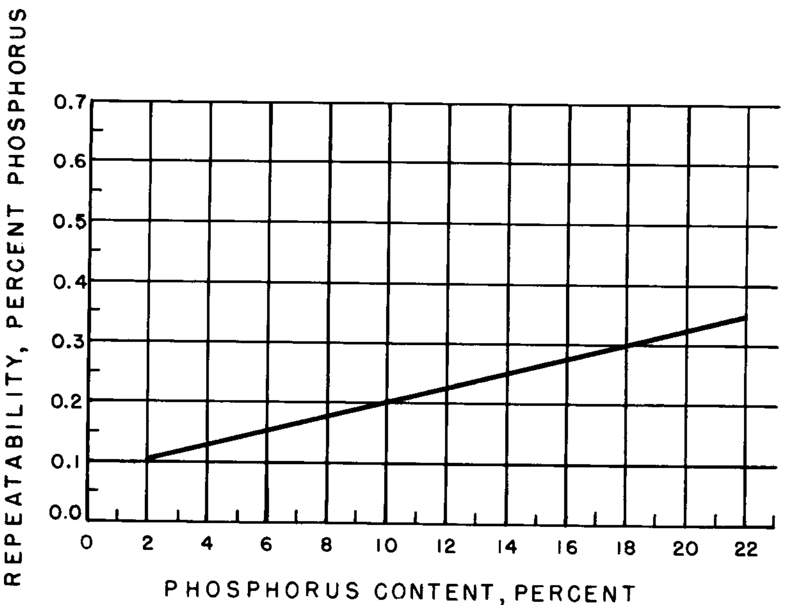

FIG. 2 Repeatability of Test Methods D1091 by Gravimetric Procedure

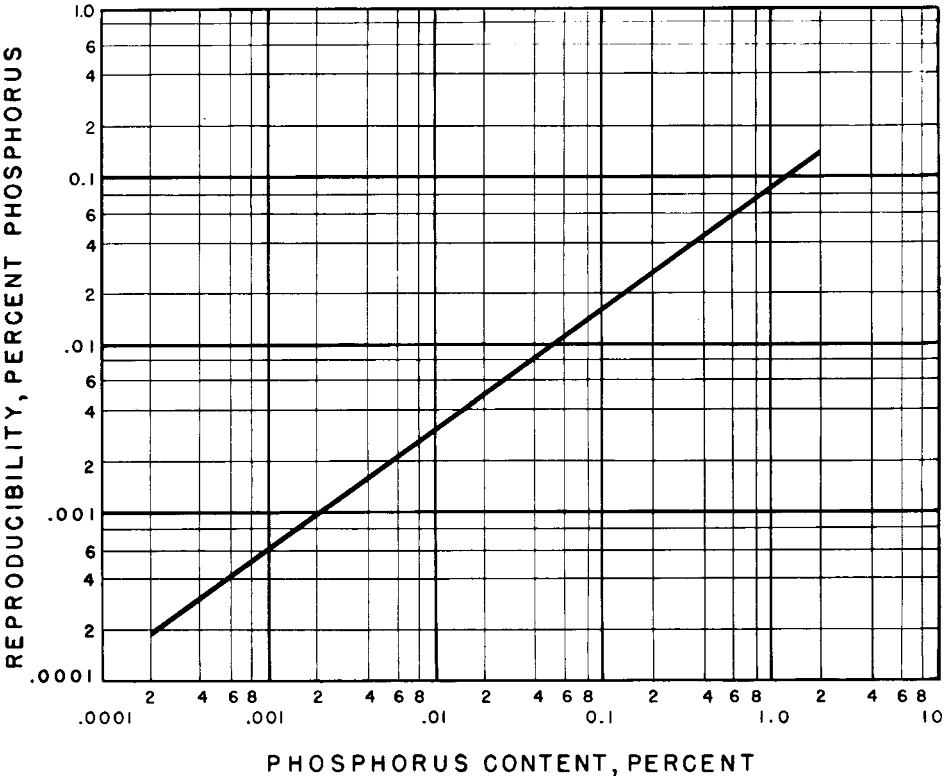

FIG. 3 Reproducibility of Test Methods D1091 by Photometric Procedure

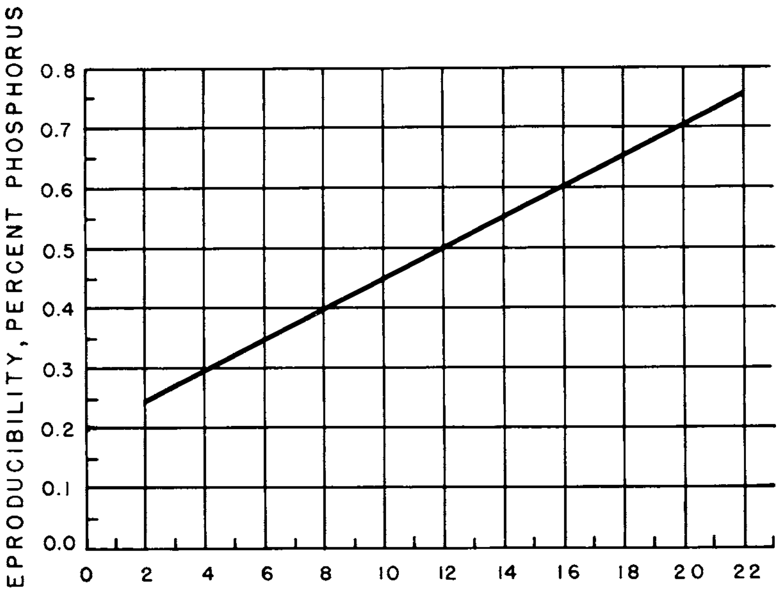

FIG. 4 Reproducibility of Test Methods D1091 by Gravimetric Procedure

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

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

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).[6,7]

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 testing process (see Practice D6299)[6,7]. 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 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.[7]

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

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[6] ASTM MNL 7: *Manual on Presentation of Data Control Chart Analysis*, 6th Ed.

[7] "TQA in the Petroleum and Lubricant Testing Laboratories." Available from ASTM Headquarters.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D1091 – 95) that may impact the use of this standard.

(*1*) Modified Section 2 to allow automatic sampling.
(*2*) Inserted QC sample in reagent sections (see 5.5, 15.5, and 22.11).
(*3*) Inserted Section 26 on QC.

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