Designation: D 3231 – 07

An American National Standard

Standard Test Method for Phosphorus in Gasoline[1]

1. Scope*

1.1 This test method covers the determination of phosphorus generally present as pentavalent phosphate esters or salts, or both, in gasoline. This test method is applicable for the determination of phosphorus in the range from 0.2 to 40 mg P/litre or 0.0008 to 0.15 g P/U.S. gal.

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

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.* For specific warning statements, see Section 6 and 9.5.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1193 Specification for Reagent Water

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

E 832 Specification for Laboratory Filter Papers

3. Summary of Test Method

3.1 Organic matter in the sample is decomposed by ignition in the presence of zinc oxide. The residue is dissolved in sulfuric acid and reacted with ammonium molybdate and hydrazine sulfate. The absorbance of the Molybdenum Blue complex is proportional to the phosphorus concentration in the sample and is read at approximately 820 nm in a 5-cm cell.

4. Significance and Use

4.1 Phosphorus in gasoline will damage catalytic convertors used in automotive emission control systems, and its level therefore is kept low.

5. Apparatus

5.1 *Buret*, 10-mL capacity, 0.05-mL subdivisions.

5.2 *Constant-Temperature Bath*, equipped to hold several 100-mL volumetric flasks submerged to the mark. Bath must have a large enough reservoir or heat capacity to keep the temperature at 82.2 to 87.8°C (180 to 190°F) during the entire period of sample heating.

NOTE 1—If the temperature of the hot water bath drops below 82.2°C (180°F), the color development cannot be complete.

5.3 *Cooling Bath*, equipped to hold several 100-mL volumetric flasks submerged to the mark in ice water.

5.4 *Filter Paper*, for quantitative analysis, Class G for fine precipitates as defined in Specification E 832.

5.5 *Ignition Dish*—Coors porcelain evaporating dish, glazed inside and outside, with pourout (Size No. 00A, diameter 75 mm, capacity 70 mL).

5.6 *Spectrophotometer*, equipped with a tungsten lamp, a red-sensitive phototube capable of operating at 830 nm and with absorption cells that have a 5-cm light path.

5.7 *Thermometer*, ASTM 34C or 34F, range from 25 to 105°C (77 to 221°F).

5.8 *Volumetric Flask*, 100-mL with ground-glass stopper.

5.9 *Volumetric Flask*, 1000-mL with ground-glass stopper.

5.10 *Syringe*, Luer-Lok, 10-mL equipped with 5-cm, 22-gauge needle.

---

[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 May 1, 2007. Published June 2007. Originally approved in 1973. Last previous edition approved in 2002 as D 3231–02.

[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.

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

6. Reagents

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.[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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types II or III of Specification D 1193.

6.3 *Ammonium Molybdate Solution*—(**Warning**—Poisonous gas may be liberated in fire. Irritating to skin and eyes. Harmful if swallowed.) (**Warning**—In addition to other precautions, wear a face shield, rubber gloves, and a rubber apron when adding concentrated sulfuric acid to water.) Using graduated cylinders for measurement, add slowly, with continuous stirring, 225 mL of concentrated sulfuric acid (H_2SO_4, relative density 1.84) to 500 mL of water contained in a beaker placed in a bath of cold water. Cool to room temperature, and add 20 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). Stir until solution is complete and transfer to a 1000-mL flask. Dilute to the mark with water.

6.4 *Hydrazine Sulfate Solution*—Dissolve 1.5 g of hydrazine sulfate (**Warning**—Cancer suspect agent.) ($H_2NNH_2\cdot H_2SO_4$) in 1 L of water, measured with a graduated cylinder. (**Warning**—This solution is not stable. Keep it tightly stoppered and in the dark. Prepare a fresh solution after 3 weeks.)

6.5 *Molybdate-Hydrazine Reagent*—Pipet 25 mL of ammonium molybdate solution into a 100-mL volumetric flask containing approximately 50 mL of water, add by pipet 10 mL of $H_2NNH_2\cdot H_2SO_4$ solution, and dilute to 100 mL with water.

NOTE 2—This reagent is unstable and is to be used within about 4 h. Prepare it immediately before use. Each determination (including the blank) uses 50 mL.

6.6 *Phosphorus, Stock Solution, Standard (1.00 mg P/mL)*—Dry approximately 5 g of potassium dihydrogen phosphate (KH_2PO_4) in an oven at 105 to 110°C (221 to 230°F) for 3 h. Dissolve 4.393 ± 0.002 g of the reagent in 150 mL, measured with a graduate cylinder, of $H_2SO_4(1 + 10)$ contained in a 1000-mL volumetric flask. Dilute with water to the mark.

6.7 *Phosphorus Solution, Standard (10.0 µg P/mL)*—Pipet 10 mL of phosphorus stock standard solution into a 1000-mL volumetric flask and dilute to the mark with water.

6.8 *Sulfuric Acid (1 + 10)*—(**Warning**—Concentrated sulfuric acid causes severe burns. Strong oxidizer.) (**Warning**—In addition to other precautions, wear a face shield, rubber gloves, and a rubber apron when adding concentrated sulfuric acid to water.) Using graduated cylinders for measurement, add slowly, with continuous stirring, 100 mL of H_2SO_4 (relative density 1.84) to 1 L of water contained in a beaker placed in a bath of cold water.

6.9 *Zinc Oxide*—(**Warning—**See 6.8.) (**Warning**—High-bulk density zinc oxide can cause spattering. Density of approximately 0.5 g/cm^3 has been found satisfactory.)

6.10 *Quality Control (QC) Samples*, preferably are 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 11.

7. Sampling

7.1 Take samples in accordance with the instructions in Practice D 4057.

7.2 Use the following table as a guide for selecting sample size:

Phosphorus, mg/L	Equivalent, g/gal	Sample Size, mL
2.5–40	0.01–0.15	1.00
1.3–20	0.005–0.075	2.00
0.9–13	0.0037–0.05	3.00
1 or less	0.0038 or less	10.0

NOTE 3—When using a 10-mL sample, ignite aliquots of 2 mL of sample in the same 2-g portion of zinc oxide; allow the zinc oxide to cool before adding the next 2-mL aliquot of gasoline (Note 5).

8. Calibration

8.1 Transfer by buret, or a volumetric transfer pipet, 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 3.5, and 4.0 mL of phosphorus standard solution into 100-mL volumetric flasks.

8.2 Pipet 10 mL of $H_2SO_4(1 + 10)$ into each flask. Mix immediately by swirling.

8.3 Prepare the molybdate-hydrazine reagent. Prepare sufficient volume of reagent based on the number of samples being analyzed.

8.4 Pipet 50 mL of the molybdate-hydrazine reagent to each volumetric flask. Mix immediately by swirling.

8.5 Dilute to 100 mL with water.

8.6 Mix well and place in the constant-temperature bath so that the contents of the flask are submerged below the level of the bath. Maintain bath temperature at 82.2 to 87.8°C (180 to 190°F) for 25 min (Note 1).

8.7 Transfer the flask to the cooling bath and cool the contents rapidly to room temperature. Do not allow the samples to cool more than 2.8°C (5°F) below room temperature.

NOTE 4—Place a chemically clean thermometer in one of the flasks to check the temperature.

8.8 After cooling the flasks to room temperature, remove them from the cooling water bath and allow them to stand for 10 min at room temperature.

8.9 Using the 2.0-mL phosphorus standard in a 5-cm cell, determine the wavelength near 820 nm that gives maximum absorbance. The wavelength giving maximum absorbance should not exceed 830 nm.

8.9.1 Using the red-sensitive phototube and 5-cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water. If using a

---

[3] *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.

dual-beam spectrophotometer, place distilled water in both cells. Use the wavelength of maximum absorbance in the determination of calibration readings and future sample readings.

8.9.2 The use of 1-cm cells for the higher concentrations is permissible.

8.10 Measure the absorbance of each calibration sample including the blank (0.0 mL phosphorus standard) at the wavelength of maximum absorbance with distilled water in the reference cell. Great care shall be taken to avoid possible contamination. If the absorbance of the blank exceeds 0.04 (for 5-cm cell), check for source of contamination. It is suggested that the results be disregarded and the test be rerun with fresh reagents and clean glassware.

8.11 Correct the absorbance of each standard solution by subtracting the absorbance of the blank (0.0 mL phosphorus standard).

8.12 Prepare a calibration curve by plotting the corrected absorbance of each standard solution against micrograms of phosphorus. One millilitre of phosphorus solution standard provides 10 µg of phosphorus.

9. Procedure

9.1 Clean all glassware before use with cleaning acid or by some procedure that does not involve use of commercial detergents. These compounds often contain alkali phosphates that are strongly adsorbed 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.

9.2 Observe the usual precautions of cleanliness, careful manipulation, and avoidance of contamination in order to obtain satisfactory accuracy with the small amounts of phosphorus involved.

9.3 Transfer 2 ± 0.2 g of zinc oxide into a conical pile in a clean, dry, unetched ignition dish.

9.4 Make a deep depression in the center of the zinc oxide pile with a stirring rod.

9.5 Pipet the gasoline sample (Note 5) (see 7.2 for suggested sample volume) into the depression in the zinc oxide. (**Warning**—In addition to other precautions, cool the ignition dish before adding the additional aliquots of gasoline to avoid a flash fire.) Record the temperature of the fuel if the phosphorus content is required at 15.6°C (60°F) and make correction as directed in 10.2.

NOTE 5—For the 10-mL sample use multiple additions and a syringe. Hold the tip of the needle at approximately ⅔ of the depth of the zinc oxide layer and slowly deliver 2 mL of the sample; fast sample delivery may give low results. Give sufficient time for the gasoline to be absorbed by the zinc oxide. Follow step 9.6. Cool the dish to room temperature. Repeat steps 9.5 and 9.8 until all the sample has been burned.

9.6 Cover the sample with a small amount of fresh zinc oxide from the reagent bottle (use the tip of a small spatula to deliver approximately 0.2 g). Tap the sides of the ignition dish to pack the zinc oxide.

9.7 Prepare the blank, using the same amount of zinc oxide in an ignition dish.

9.8 Ignite the gasoline, using the flame from a Bunsen burner. Allow the gasoline to burn to extinction (Note 5).

9.9 Place the ignition dishes containing the sample and blank in a hot muffle furnace set at a temperature of 621 to 704°C (1150 to 1300°F) for 10 min. Remove and cool the ignition dishes. When cool gently tap the sides of the dish to loosen the zinc oxide. Again place the dishes in the muffle furnace for 5 min. Remove and cool the ignition dishes to room temperature. The above treatment is usually sufficient to burn the carbon. If the carbon is not completely burned off, place the dish into the furnace for further 5-min periods.

NOTE 6—Step 9.9 can also be accomplished by heating the ignition dish with a Meker burner, gradually increasing the intensity of heat until the carbon from the sides of the dish has been burned; cool to room temperature.

9.10 Pipet 25 mL of H_2SO_4 (1 + 10) into each ignition dish. While pipeting, carefully wash all traces of zinc oxide from the sides of the ignition dish.

9.11 Cover the ignition dish with a borosilicate watch glass and warm the ignition dish on a hot plate until the zinc oxide is completely dissolved.

9.12 Transfer the solution through filter paper to a 100-mL volumetric flask. Rinse the watch glass and the dish several times with distilled water (do not exceed 25 mL) and transfer the washings through the filter paper to the volumetric flask.

9.13 Prepare the molybdate-hydrazine reagent.

9.14 Add 50 mL of the molybdate-hydrazine reagent by pipet to each 100-mL volumetric flask. Mix immediately by swirling.

9.15 Dilute to 100 mL with water and mix well. Remove stoppers from flasks after mixing.

9.16 Place the 100-mL flasks in the constant-temperature bath for 25 min so that the contents of the flasks are below the liquid level of the bath. The temperature of the bath should be 82.2 to 87.8°C (180 to 190°F) (Note 1).

9.17 Transfer the 100-mL flasks to the cooling bath and cool the contents rapidly to room temperature (Note 4).

9.18 Allow the samples to stand at room temperature before measuring the absorbance.

NOTE 7—The color developed is stable for at least 4 h.

9.19 Set the spectrophotometer to the wavelength of maximum absorbance as determined in 8.9. Adjust the spectrophotometer to zero absorbance, using distilled water. If using a dual-beam spectrophotometer, place distilled water in both cells.

9.20 Measure the absorbance of the samples at the wavelength of maximum absorbance. If using a dual-beam spectrophotometer, measure the absorbance of the samples at the wavelength of maximum absorbance with distilled water in the reference cell.

9.21 Subtract the absorbance of the blank from the absorbance of each sample (8.10).

9.22 Determine the micrograms of phosphorus in the sample, using the calibration curve from 8.12 and the corrected absorbance.

10. Calculations

10.1 Calculate the milligrams of phosphorus per litre of sample as follows:

$$P, \text{ mg/L} = P/V \quad (1)$$

where:

P = phosphorus read from calibration curve, µg and

V = gasoline sample, mL.

To convert to grams of phosphorus per U.S. gallon of sample, multiply mg P/L by 0.0038.

10.2 If the gasoline sample was taken at a temperature other than 15.6°C (60°F), make the following temperature correction:

$$\text{mg } P\text{/L at } 15.6°\text{C} = [\text{mg } P\text{/L at } t][1 + 0.001\,(t - 15.6)] \quad (2)$$

where:

t = observed temperature of the gasoline, °C.

10.3 Concentrations below 2.5 mg/L or 0.01 g/gal should be reported to the nearest 0.01 mg/L or 0.0001 g/U.S. gal.

10.3.1 For higher concentrations, report results to the nearest 1 mg P/L or 0.005 g P/U.S. gal.

11. Quality Control

11.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (6.10).

11.2 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 D 6299 and ASTM MNL 7).[4]

11.3 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 D 6299 and ASTM MNL 7).[4] 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.

11.4 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.

11.5 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. See Practice D 6299 and ASTM MNL 7.[4] for further guidance on QC and control charting techniques.

12. Precision and Bias

12.1 The precision of this method was obtained by statistical examination of interlaboratory test results.

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 only in one case in twenty.

Phosphorus Content, mg/L	Repeatability
0.2 to 1.3	0.05
1.3 to 40	7 % of the mean

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 only in one case in twenty.

Phosphorus Content, mg/L	Reproducibility
0.2 to 1.3	0.13
1.3 to 40	13 % of the mean

12.2 *Bias*—The bias of this test method cannot be determined since an appropriate standard reference material containing a known amount of phosphorus in gasoline is not available to form the basis of a bias study.

13. Keywords

13.1 gasoline; phosphorous; spectrophotometer

---

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

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 3231-02) that may impact the use of this standard.

(*1*) Updated 12.2 to indicate that a standard reference gasoline sample is not available for a bias study.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).