Designation: D3231 – 18

Standard Test Method for Phosphorus in Gasoline[1]

This standard is issued under the fixed designation D3231; 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 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 mg to 40 mg P/L or 0.0008 g to 0.15 g P/U.S. gal.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Section 6 and 9.5.

1.4 *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

E832 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 °C to 87.8 °C (180 °F 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 E832.

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 °C to 105 °C (77 °F to 221 °F).

NOTE 2—Other temperature measuring devices, such as thermocouples or resistance thermometers, may be used when the temperature readings obtained by these devices are determined to produce the same results that are obtained when mercury-in-glass thermometers are used. The precision

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum 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.

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

and bias given in Section 12 may or may not apply in such cases since the published precision is based on an interlaboratory study where only mercury-in-glass thermometers were used. No information on the effect on precision when using alternative temperature measuring devices is available.

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.

5.11 *Pipets,* or equivalent volume dispensing devices, for delivering the necessary volumes of dilute sulfuric acid (6.8) and molybdate-hydrazine reagent used in this test.

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 D1193.

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 3—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 °C to 110 °C (221 °F to 230 °F) for 3 h. Dissolve 4.393 g ± 0.002 g of the reagent in 150 mL, measured with a graduate cylinder, of dilute sulfuric acid (6.8) 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 *Dilute Sulfuric Acid (one part H_2SO_4 and 10 parts water)*—(**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 Practices D4057 or D4177.

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 4—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 6).

8. Calibration

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

8.2 Dispense 10 mL of dilute sulfuric acid (6.8) 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 Dispense 50 mL of the molybdate-hydrazine reagent into each volumetric flask. Mix immediately by swirling.

8.5 Dilute to 100 mL with water.

[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.