



Designation: ~~D3231~~—~~13~~ D3231 – 18

## Standard Test Method for Phosphorus in Gasoline<sup>1</sup>

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 ( $\epsilon$ ) 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 ~~0-20.2 mg~~ 0.0080-0.0008 g to ~~0-15 g~~ 0-0.15 g P/U.S. gal.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses ~~are for information only 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~~ safety, health, and ~~health~~ 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:*<sup>2</sup>

[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~~ 820 nm in a ~~5-cm~~ 5 cm cell.

### 4. Significance and Use

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

### 5. Apparatus

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

5.2 *Constant-Temperature Bath*, equipped to hold several ~~100-mL~~ 100 mL volumetric flasks submerged to the mark. Bath must have a large enough reservoir or heat capacity to keep the temperature at ~~82.282.2 °C~~ 82.282.2 °C to ~~87.8°C~~ 87.8°C (~~180°F~~ 180 °F to ~~190°F~~ 190 °F) during the entire period of sample heating.

<sup>1</sup> 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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<sup>2</sup> 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

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

5.3 *Cooling Bath*, equipped to hold several ~~100-mL~~ 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~~); 75 mm, capacity 70 mL).

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

5.7 *Thermometer*, ASTM 34C or 34F, range from ~~25-25 °C~~ to ~~105°C (77-105 °C (77 °F to 221°F))~~; 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 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~~ 100 mL with ground-glass stopper.

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

5.10 *Syringe*, Luer-Lok, ~~10-mL~~ 10 mL equipped with ~~5-cm, 22-gauge~~ 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.<sup>3</sup> 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—Warning~~ **Poisonous—Poisonous** gas may be liberated in fire. Irritating to skin and eyes. Harmful if swallowed.) (~~Warning—Warning~~ **In—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~~ 225 mL of concentrated sulfuric acid ( $H_2SO_4$ , relative density 1.84) to ~~500 mL~~ 500 mL of water contained in a beaker placed in a bath of cold water. Cool to room temperature, and add ~~20 g~~ 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~~ 1000 mL flask. Dilute to the mark with water.

6.4 *Hydrazine Sulfate Solution*—Dissolve ~~1.5 g~~ 1.5 g of hydrazine sulfate (~~Warning—Warning~~ **Cancer—Cancer** suspect agent.) ( $H_2NNH_2 \cdot H_2SO_4$ ) in ~~1 L~~ 1 L of water, measured with a graduated cylinder. (~~Warning—Warning~~ **This—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~~ 25 mL of ammonium molybdate solution into a ~~100-mL~~ 100 mL volumetric flask containing approximately ~~50 mL~~ 50 mL of water, add by pipet ~~10 mL~~ 10 mL of  $H_2NNH_2 \cdot H_2SO_4$  solution, and dilute to ~~100 mL~~ 100 mL with water.

NOTE 3—This reagent is unstable and is to be used within about ~~4 h~~ 4 h. Prepare it immediately before use. Each determination (including the blank) uses ~~50 mL~~ 50 mL.

6.6 *Phosphorus, Stock Solution, Standard* (~~1.00 mg~~ 1.00 mg P/mL)—Dry approximately ~~5 g~~ 5 g of potassium dihydrogen phosphate ( $KH_2PO_4$ ) in an oven at ~~105-105 °C~~ to ~~110°C (221-110 °C (221 °F to 230°F))~~ 230 °F for ~~3 h~~ 3 h. Dissolve ~~4.3934.393 g~~  $\pm 0.002 g$  0.002 g of the reagent in ~~150 mL~~ 150 mL, measured with a graduate cylinder, of dilute sulfuric acid (6.8) contained in a ~~1000-mL~~ 1000 mL volumetric flask. Dilute with water to the mark.

6.7 *Phosphorus Solution, Standard* (10.0  $\mu g$  P/mL)—Pipet ~~10 mL~~ 10 mL of phosphorus stock standard solution into a ~~1000-mL~~ 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—Warning~~ **Concentrated—Concentrated** sulfuric acid causes severe burns. Strong oxidizer.) (~~Warning—Warning~~ **In—In** addition to other precautions, wear a face shield, rubber gloves,

<sup>3</sup> *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.

and a rubber apron when adding concentrated sulfuric acid to water.) Using graduated cylinders for measurement, add slowly, with continuous stirring, ~~100 mL~~ 100 mL of H<sub>2</sub>SO<sub>4</sub> (relative density 1.84) to ~~1 L~~ 1 L of water contained in a beaker placed in a bath of cold water.

6.9 *Zinc Oxide*—(~~Warning—Warning—See 6.8.~~) (~~Warning—Warning~~~~High-bulk—High-bulk~~ density zinc oxide can cause spattering. Density of approximately ~~0.5–0.5 g/cm<sup>3</sup>~~ 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~~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~~ 10 mL sample, ignite aliquots of ~~2 mL~~ 2 mL of sample in the same ~~2-g~~ 2 g portion of zinc oxide; allow the zinc oxide to cool before adding the next ~~2 mL~~ 2 mL aliquot of gasoline (Note 6).

## 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~~ 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~~ 100 mL volumetric flasks.

8.2 Dispense ~~10 mL~~ 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~~ 50 mL of the molybdate-hydrazine reagent into each volumetric flask. Mix immediately by swirling.

8.5 Dilute to ~~100 mL~~ 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 ~~82–82.2 °C~~ 82.2 °C to ~~87–8 °C~~ 87.8 °C (~~180 °F~~ 180 °F to ~~190 °F~~ 190 °F) for ~~25 min~~ 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~~ 2.8 °C (~~5 °F~~ 5 °F) below room temperature.

NOTE 5—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~~ 10 min at room temperature.

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

8.9.1 Using the red-sensitive phototube and ~~5-cm~~ 5 cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water. If using a 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~~ 1 cm cells for the higher concentrations is permissible.

8.10 Measure the absorbance of each calibration sample including the blank (~~0.0 mL~~ 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~~ 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~~ 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~~ 10 µg of phosphorus.