

**§ 80.1468**

**40 CFR Ch. I (7–1–11 Edition)**

by that person's immediate designee, and shall contain the following declaration:

"I hereby certify: (1) That I have actual authority to sign on behalf of and to bind [INSERT NAME OF FOREIGN RIN OWNER] with regard to all statements contained herein; (2) that I am aware that the information contained herein is being Certified, or submitted to the United States Environmental Protection Agency, under the requirements of 40 CFR part 80, subpart M, and that the information is material for determining compliance under these regulations; and (3) that I have read and understand the information being Certified or submitted, and this information is true, complete and correct to the best of my knowledge and belief after I have taken reasonable and appropriate steps to verify the accuracy thereof. I affirm that I have read and understand the provisions of 40 CFR part 80, subpart M, including 40 CFR 80.1467 apply to [INSERT NAME OF FOREIGN RIN OWNER]. Pursuant to Clean Air Act section 113(c) and 18 U.S.C. 1001, the penalty for furnishing false, incomplete or misleading information in this certification or submission is a fine of up to \$10,000 U.S., and/or imprisonment for up to five years."

**§ 80.1468 Incorporation by reference.**

(a) Certain material is incorporated by reference into this part with the approval of the Director of the Federal Register under 5 U.S.C. 552(a) and 1 CFR part 51. To enforce any edition other than that specified in this section, the Environmental Protection Agency (EPA) must publish notice of change in the FEDERAL REGISTER and the material must be available to the public. All approved material is available for inspection at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030 or go to: [http://www/archives.gov/federal\\_register/code\\_of\\_federal\\_regulations/ibr\\_locations.html](http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html). This material is also available for inspection at the EPA Docket Center, Docket No. EPA-HQ-OAR-2005-0161, EPA/DC, EPA West, Room 3334, 1301 Constitution Ave., NW., Washington DC. The telephone number

for the Air Docket is (202) 566-1742. Also, this material is available from the source listed in paragraph (b) of this section.

(b) American Society for Testing and Materials, 100 Barr Harbor Drive, P.O. Box C-700, West Conshohocken, Pennsylvania 19428 (1-800-262-1373, [www.astm.org](http://www.astm.org)).

(1) ASTM D 1250-08 ("ASTM D 1250"), Standard Guide for Use of the Petroleum Measurement Tables, Approved 2008; IBR approved for § 80.1426(f)(8)(ii)(B).

(2) ASTM D 4442-07 ("ASTM D 4442"), Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Base Materials, Approved 2007; IBR approved for § 80.1426(f)(7)(v)(B).

(3) ASTM D 4444-08 ("ASTM D 4444"), Standard Test Method for Laboratory Standardization and Calibration of Hand-Held Moisture Meters, Approved 2008; IBR approved for § 80.1426(f)(7)(v)(B).

(4) ASTM D 6751-09 ("ASTM D 6751"), Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, Approved 2009; IBR approved for § 80.1401.

(5) ASTM D 6866-08 ("ASTM D 6866"), Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis, Approved 2008; IBR approved for §§ 80.1426(f)(9)(ii) and 80.1430(e)(2).

(6) ASTM E 711-87 ("ASTM E 711"), Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter, Reapproved 2004; IBR approved for § 80.1426(f)(7)(v)(A).

(7) ASTM E 870-82 ("ASTM E 870"), Standard Test Methods for Analysis of Wood Fuels, Reapproved 2006; IBR approved for § 80.1426(f)(7)(v)(A).

**APPENDIX A TO PART 80—TEST FOR THE DETERMINATION OF PHOSPHORUS IN GASOLINE**

*1. Scope.*

1.1 This method was developed for the determination of phosphorus generally present as pentavalent phosphate esters or salts, or both, in gasoline. This method is applicable for the determination of phosphorus in the

range from 0.0008 to 0.15 g P/U.S. gal, or 0.2 to 49 mg P/liter.

## 2. Applicable documents.

### 2.1 ASTM Standards:

D 1100 Specification for Filter Paper for Use in Chemical Analysis.

## 3. Summary of 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. Apparatus.

4.1 Buret, 10-ml capacity, 0.05-ml subdivisions.

4.2 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 180 to 190 °F (82.2 to 87.8 °C) during the entire period of sample heating.

NOTE 1: If the temperature of the hot water bath drops below 180 °F (82.2 °C) the color development may not be complete.

4.3 Cooling Bath, equipped to hold several 100-ml volumetric flasks submerged to the mark in ice water.

4.4 Filter Paper, for quantitative analysis, Class G for fine precipitates as defined in Specification D 1100.

4.5 Ignition Dish—Coors porcelain evaporating dish, glazed inside and outside, with pourout (size no. 00A, diameter 75 mm, capacity 70 ml).

4.6 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.

4.7 Thermometer, range 50 to 220 °F (10 to 105 °C).

4.8 Volumetric Flask, 100-ml with ground-glass stopper.

4.9 Volumetric Flask, 1000-ml with ground-glass stopper.

4.10 Syringe, Luer-Lok, 10-ml equipped with 5-cm. 22-gage needle.

## 5. Reagents.

5.1 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. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high pu-

rity 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 distilled water or water of equal purity.

5.3 Ammonium Molybdate Solution—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 225 ml of concentrated sulfuric acid 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<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub> O<sub>24</sub>·4H<sub>2</sub>O). Stir until solution is complete and transfer to a 1000-ml flask. Dilute to the mark with water.

NOTE 2: Wear a face shield, rubber gloves, and a rubber apron when adding concentrated sulfuric acid to water.

5.4 Hydrazine Sulfate Solution—Dissolve 1.5 of hydrazine sulfate (H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>) in 1 litre of water, measured with a graduated cylinder.

NOTE 3: This solution is not stable. Keep it tightly stoppered and in the dark. Prepare a fresh solution after 3 weeks.

5.5 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 N<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub> solution, and dilute to 100 ml with water.

NOTE 4: This reagent is unstable and should be used within about 4 h. Prepare it immediately before use. Each determination (including the blank) uses 50 ml.

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

5.7 Phosphorus, Stock Standard Solution (1.00 mg P/ml)—Dry approximately 5 g of potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) in an oven at 221 to 230 °F (105 to 110 °C) for 3 h. Dissolve 4.393 ± 0.002 g of the reagent in 150 ml, measured with a graduated cylinder, of H<sub>2</sub>SO<sub>4</sub>(1+10) contained in a 1000-ml volumetric flask. Dilute with water to the mark.

5.8 Sulfuric Acid (1+10)—Using graduated cylinders for measurement add slowly (Note 2), with continuous stirring, 100-ml of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to 1 litre of water contained in a beaker placed in a bath of cold water.

5.9 Zinc Oxide.

NOTE 5: High-bulk density zinc oxide may cause spattering. Density of approximately 0.5 g/cm<sup>3</sup> has been found satisfactory.

## 6. Calibration.

6.1 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.

6.2 Pipet 10 ml of H<sub>2</sub> SO<sub>4</sub> (1+10) into each flask. Mix immediately by swirling.

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

6.4 Pipet 50 ml of the molybdate-hydrazine solution to each volumetric flask. Mix immediately by swirling.

6.5 Dilute to 100 ml with water.

6.6 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 180 to 190 °F (82.2 to 87.8 °C) for 25 min (Note 1).

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

NOTE 6: Place a chemically clean thermometer in one of the flasks to check the temperature.

6.8 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.

6.9 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.

6.9.1 Using a red-sensitive phototube and 5-cm cells, adjust the spectrophotometer to zero absorbance at the wavelength of maximum absorbance using distilled water in both cells. Use the wavelength of maximum absorbance in the determination of calibration readings and future sample readings.

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

6.10 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.

NOTE 7: Great care must 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.

6.11 Correct the absorbance of each standard solution by subtracting the absorbance of the blank (0 ml phosphorus standard).

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

#### 7. Sampling.

7.1 Selection of the size of the sample to be tested depends on the expected concentration of phosphorus in the sample. If a con-

centration of phosphorus is suspected to be less than 0.0038 g/gal (1.0 mg/litre), it will be necessary to use 10 ml of sample.

NOTE 8: Two grams of zinc oxide cannot absorb this volume of gasoline. Therefore the 10-ml sample is ignited in aliquots of 2 ml in the presence of 2 g of zinc oxide.

7.2 The following table serves as a guide for selecting sample size:

Phosphorus, milligrams per liter	Equivalent, grams per gallon	Sample size, milliliter
2.5 to 40 .....	0.01 to 0.15 .....	1.00
1.3 to 20 .....	0.005 to 0.075 .....	2.00
0.9 to 13 .....	0.0037 to 0.05 .....	3.00
1 or less .....	0.0038 or less .....	10.00

#### 8. Procedure.

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

NOTE 9: In order 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 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.

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

8.3 Pipet the gasoline sample (Note 10) (see 7.2 for suggested sample volume) into the depression in the zinc oxide. Record the temperature of the fuel if the phosphorus content is required at 60 °F (15.6 °C) and make correction as directed in 9.2.

NOTE 10: For the 10-ml sample use multiple additions and a syringe. Hold the tip of the needle at approximately ¾ 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 8.6. Cool the dish to room temperature. Repeat steps 8.3 and 8.6 until all the sample has been burned. Safety—cool the ignition dish before adding the additional aliquots of gasoline to avoid a flash fire.

8.4 Cover the sample with a small amount of fresh zinc oxide from 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.

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

8.6 Ignite the gasoline, using the flame from a bunsen burner. Allow the gasoline to burn to extinction (NOTE 10).

8.7 Place the ignition dishes containing the sample and blank in a hot muffle furnace set at a temperature of 1150 to 1300 °F (621 to 704 °C) 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 oven for further 5-min. periods.

NOTE 11: Step 8.7 may 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, then cool to room temperature.

8.8 Pipet 25 ml of H<sub>2</sub> SO<sub>4</sub> (1+10) to each ignition dish. While pipeting, carefully wash all traces of zinc oxide from the sides of the ignition dish.

8.9 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.

8.10 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.

8.11 Prepare the molybdate-hydrazine solution.

8.12 Add 50 ml of the molybdate-hydrazine solution by pipet to each 100-ml volumetric flask. Mix immediately by swirling.

8.13 Dilute to 100 ml with water and mix well. Remove stoppers from flasks after mixing.

8.14 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 180 to 190 °F (82.2 to 87.8 °C) (NOTE 1).

8.15 Transfer the 100-ml flasks to the cooling bath and cool the contents rapidly to room temperature (NOTE 6).

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

NOTE 12: The color developed is stable for at least 4 h.

8.17 Set the spectrophotometer to the wavelength of maximum absorbance as determined in 6.9. Adjust the spectrophotometer to zero absorbance, using distilled water in both cells.

8.18 Measure the absorbance of the samples at the wavelength of maximum absorbance with distilled water in the reference cell.

8.19 Subtract the absorbance of the blank from the absorbance of each sample (NOTE 7).

8.20 Determine the micrograms of phosphorous in the sample, using the calibration curve from 6.12 and the corrected absorbance.

#### 9. Calculations.

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

$$P, \text{ mg/litre} = P/V$$

where:

P = micrograms of phosphorus read from calibration curve, and

V = millilitres of gasoline sample.

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

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

$$\text{mg P/litre at } 15.6 \text{ } ^\circ\text{C} = [\text{mg P/litre at } t] [1+0.001(t-15.6)]$$

where:

t = observed temperature of the gasoline, °C.

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

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

#### 10. Precision.

10.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

10.2 Repeatability—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

g P/U.S. gal (mg-P/litre)	Repeatability
0.0008 to 0.005 (0.2 to 1.3) ..	0.0002 g P/U.S. gal (0.05 mg P/litre).
0.005 to 0.15 (1.3 to 40) .....	7% of the mean.

10.3 Reproducibility—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

g P/U.S. gal (mg-P/litre)	Reproducibility
0.0008 to 0.005 (0.2 to 1.3) ..	0.0005 g P/U.S. gal (0.13 mg P/litre).
0.005 to 0.15 (1.3 to 40) .....	13% of the mean.

[39 FR 24891, July 8, 1974; 39 FR 25653, July 12, 1974]