

Phosphorus, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, dissolved, I-2600-85 (mg/L as P): 00666

Phosphorus, total, I-4600-85 (mg/L as P): 00665

Phosphorus, total-in-bottom-material, dry wt, I-6600-85 (mg/kg as P): 00668

1. Application

1.1 This method may be used to analyze most water, wastewater, brines, and water-suspended sediment containing from 0.01 to 1.0 mg/L of phosphorus. Samples containing greater concentrations need to be diluted.

1.2 This method may be used to analyze bottom material containing from 40 to 4,000 mg/kg of phosphorus. This range may be extended by using a 0.1-g subsample rather than the 1-g subsample specified.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which, upon reduction with ascorbic acid, produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966).

2.3 Mercuric chloride-preserved water samples and water-suspended sediment mixtures are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

2.4 Digested and centrifuged bottom-material samples are diluted to reduce the acid and phosphorus concentrations before final analysis.

3. Interferences

3.1 The color of the molybdate blue complex is strongly affected by pH. The method incorporates a dilution step for bottom-material

samples to reduce the hydrogen-ion concentrations of all samples.

3.2 Barium, lead, and silver interfere by forming a phosphate precipitate, but the effect is usually negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.3 Arsenic as arsenate (AsO_4^{3-}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 $\mu\text{g/L}$ do not interfere. Greater concentrations were not investigated.

4. Apparatus

4.1 *Autoclave.*

4.2 *Centrifuge.*

4.3 *Centrifuge tubes, 50-mL capacity.*

4.4 *Glass tubes with plastic caps, disposable, 18×150 mm.*

4.5 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.6 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L P:

Absorption cell ----- 50 mm

Wavelength ----- 880 nm or 660 nm

Cam ----- 40/h (5/1)

Heating-bath temperature ----- 37.5°C

5. Reagents

5.1 *Ammonium molybdate solution*, 35.6 g/L: Dissolve 40 g ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid solution*, 18 g/L: Dissolve 18 g ascorbic acid $(\text{C}_6\text{H}_8\text{O}_6)$ in 800 mL demineralized water and dilute to 1 L. Keep in a dark bottle and refrigerate. The solution is stable for 1 week.

5.3 *Antimony potassium tartrate solution*, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent*: Combine reagents in order and volumes listed below. This reagent is stable for about 8 h.

Sulfuric acid, 2.45M - 50 mL

Ammonium molybdate

solution ----- 15 mL

Ascorbic acid solution 30 mL

Antimony potassium

tartrate solution -- 5 mL

5.5 *Levor V solution* or equivalent.

5.6 *Phosphate standard solution I*, 1.00 mL = 0.100 mg P: Dissolve 0.4394 g KH_2PO_4 , dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 *Phosphate standard solution II*, 1.00 mL = 0.010 mg P: Dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 *Phosphate working standards*: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II with demineralized water. Dissolve 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

| Phosphate standard solution II (mL) | Orthophosphate-phosphorus concentration (mg/L) |
|--|--|
| 0.0 | 0.00 |
| 1.0 | .05 |
| 2.0 | .10 |
| 5.0 | .25 |
| 10 | .50 |
| 20 | 1.00 |

5.9 *Potassium persulfate*, crystals.

5.10 *Potassium persulfate solution*, 4 g/L: Dissolve 4.0 g $\text{K}_2\text{S}_2\text{O}_8$ in demineralized water and dilute to 1 L.

5.11 *Sulfuric acid*, concentrated (sp gr 1.84).

5.12 *Sulfuric acid*, 2.45M: *Cautiously*, add slowly, with constant stirring and cooling, 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water and dilute to 1 L with demineralized water.

5.13 *Sulfuric acid*, 0.45M: *Cautiously*, add slowly, with constant stirring and cooling, 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water and dilute to 1 L with demineralized water.

5.14 *Sulfuric acid-persulfate reagent*, (1 + 1): Mix equal volumes of 0.45M sulfuric acid and potassium persulfate solution.

5.15 *Water diluent*: Dissolve 20g NaCl in 800 mL demineralized water. Add 2.0 mL Levor V and dilute to 1L with demineralized water.

6. Procedure

6.1 Follow instructions in paragraphs 6.1.1 through 6.1.4 for water or water-suspended sediment and in paragraphs 6.1.5 through 6.1.12 for bottom material.

6.1.1 Pipet a volume of well-mixed sample containing less than 0.01 mg total P (10.0 mL max) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.1.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

6.1.3 Add 4.0 mL sulfuric acid-persulfate reagent.

6.1.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter those samples containing sediment through a 0.45- μm membrane filter. Proceed to paragraph 6.2.

6.1.5 Accurately weigh a portion of as-received sample having a dry weight of approx 1 g. The sample must first be prepared as directed in method P-0810. Transfer the weighed sample to a 50-mL centrifuge tube and add 10 mL demineralized water.

6.1.6 On a separate portion, determine the dry weight of the sample (method P-0590).

6.1.7 Add 1.0 mL concentrated H_2SO_4 and 1.0 g potassium persulfate to each centrifuge tube.

6.1.8 Autoclave for 30 min at 15 psi pressure.

6.1.9 Centrifuge for 5 to 10 min at 5,000 rpm.

6.1.10 Transfer the supernatant solution to a 200-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.11 Wash the residue several times with demineralized water, adding the washings to the volumetric flask. Dilute to 200 mL with demineralized water.

6.1.12 Pipet 5.0 mL of sample, into a 100-mL volumetric flask and dilute to volume with demineralized water. Proceed to paragraph 6.2 (NOTE 1).

NOTE 1. Use blank and standards as prepared in paragraphs 6.1.2 through 6.1.4.

6.2 Set up manifold (fig. 37).

6.3 Allow colorimeter, recorder, and heating bath to warm for at least 30 min or until the temperature of the heating bath is 37.5°C.

6.4 Adjust the baseline to read zero scale divisions on the recorder for all reagents, but with demineralized water in the sample line.

6.5 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and

subsequent sample trays. Fill remainder of each tray with unknown samples.

6.6 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of dissolved or total phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Compute total phosphorus concentrations in each bottom-material sample as follows:

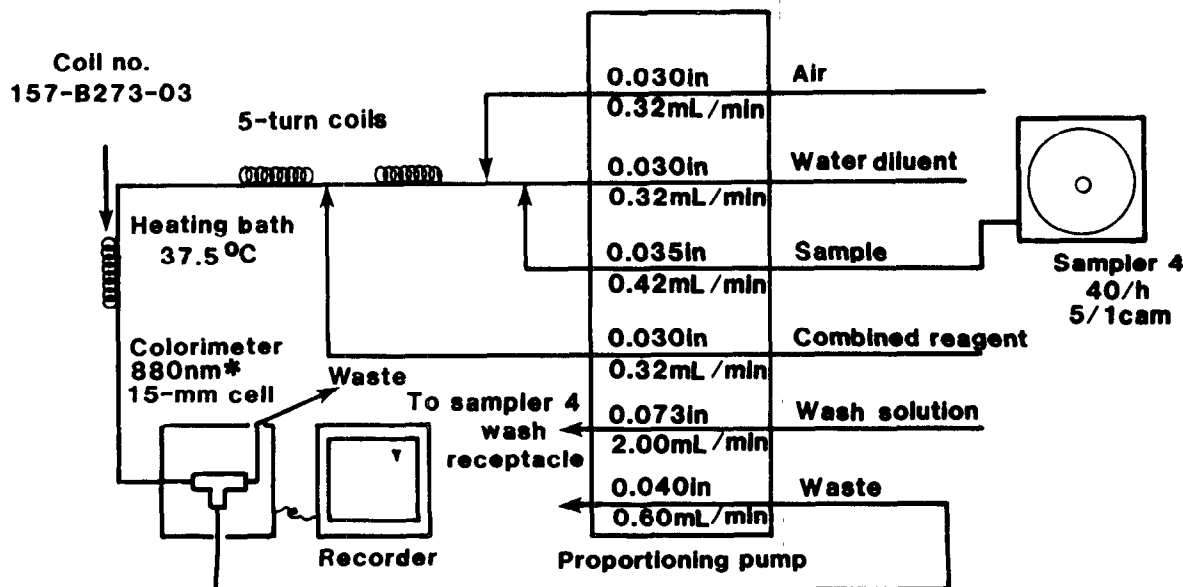
$$\text{Phosphorus (mg/kg)} = \frac{P}{5} \times \frac{20}{W} \times 1,000$$

where

P = concentration of phosphorus, milligrams per liter, in the sample,

and

W = dry weight, grams, of the sample.



* Alternatively 660 nm

Figure 37.—Phosphorus, phosphomolybdate manifold

8. Report

8.1 Report phosphorus, dissolved (00666), and total (00665), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

8.2 Report phosphorus, total-in-bottom-material (00668), in milligrams per kilogram, to two significant figures.

9. Precision

9.1 Precision for dissolved phosphorus for 20 samples within the range of 0.183 to 3.59 mg/L may be expressed as follows:

$$S_T = 0.189 X - 0.062$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of phosphorus, milligrams per liter.

The correlation coefficient is 0.9260.

9.2 Precision for dissolved phosphorus for four of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean (mg/L) | Relative standard deviation (percent) |
|------------------------|-------------|---------------------------------------|
| 3 | 0.183 | 12 |
| 13 | .572 | 8 |
| 18 | 1.411 | 9 |
| 15 | 3.59 | 19 |

9.3 It is estimated that the percent relative standard deviation for total phosphorus and for total phosphorus in bottom material will be greater than that reported for dissolved phosphorus.

References

- Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363-8.
- Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31-6.