Phosphorus, orthophosphate plus hydrolyzable, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:
Phosphorus, orthophosphate plus hydrolyzable, dissolved, I-2602-85 (mg/L as P): 00677
Phosphorus, orthophosphate plus hydrolyzable, total, I-4602-85 (mg/L as P): 00678

1. Application

This method may be used to analyze most water, brines, and water-suspended sediment containing between 0.01 and 1.0 mg/L combined acid hydrolyzable and orthophosphate-phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 Polyphosphates $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc., and a few organic phosphorus compounds are converted to orthophosphate by an acid hydrolysis.

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 samples are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 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 slight 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.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

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 µg/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyxer II,* consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L combined hydrolyzable and orthophosphate phosphorus:

Absorption cell -------- 50 mm
Wavelength ---------- 880 nm or 660 nm
Cam ---------- 40/h (5/1)
Heating-bath
temperature --------- 37.5°C

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

5. Reagents

5.1 *Ammonium molybdate solution,* 35.6 g/L: Dissolve 40 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid solution,* 18 g/L: Dissolve 18 g ascorbic acid $(C_6H_8O_6)$ in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate solution,* 3 g/L: Dissolve 3.0 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot {}^1/_2H_2O$, 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, 2.45*M* -------- 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. 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	0.05
2.0	0.10
5.0	0.25
10.0	0.50
20.0	1.00

5.9 *Sulfuric acid,* 2.45*M*: *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.

5.10 *Sulfuric acid,* 0.45*M*: *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.

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

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.01 mg combined hydrolyzable and orthophosphate-phosphorus (10.0 mL max) into a disposable glass tube and adjust the volume to 10.0 mL.

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

6.3 Add 2.0 mL 0.45*M* sulfuric acid.

6.4 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.

6.5 Set up manifold (fig. 1).

6.6 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.

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

6.8 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.

6.9 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 peak 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.

8. Report

Report phosphorus, orthophosphate plus hydrolyzable, dissolved (00677), and total (00678), concentrations as follows: less than 1

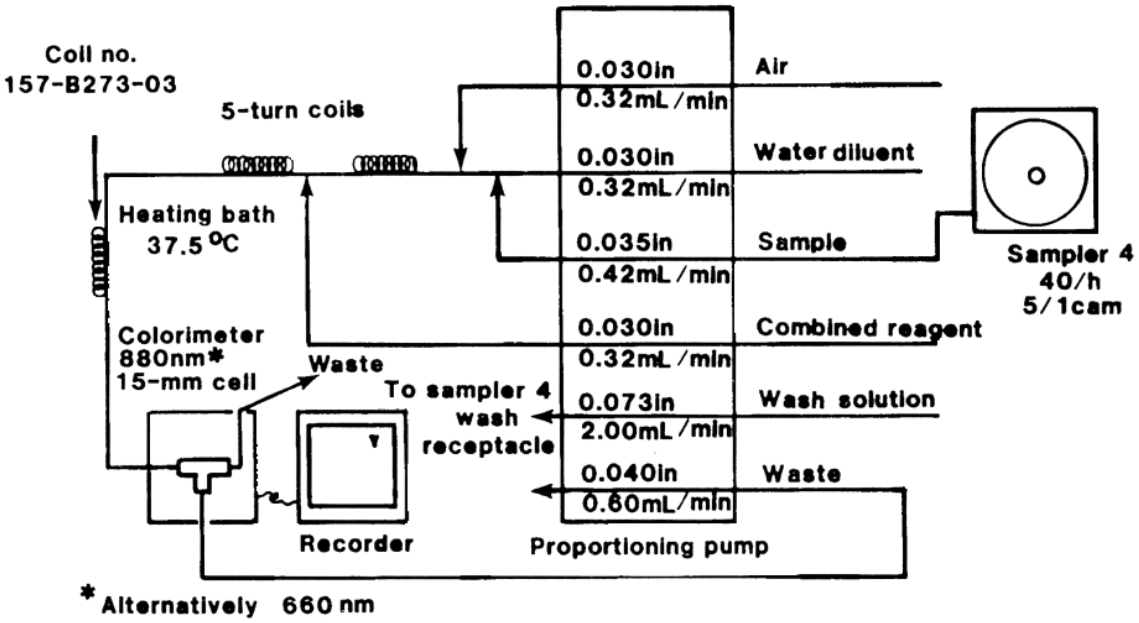

Figure 1. - Phosphorus, phosphomolybdate manifold

mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for dissolved and total orthophosphate plus hydrolyzable phosphorus will be equal to that reported for phosphorus by the automated phosphomolybdate method.

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.