Phosphorus, orthophosphate, low ionic-strength water, colorimetry, phosphomolybdate, automated-segmented flow

Parameter and code:
Phosphorus, orthophosphate, dissolved, I-2606-89 (mg/L as P): 00671

1. Application

This method is used to analyze samples of precipitation or natural water with a specific conductance of less than 100 μS/cm containing from 0.001 to 0.20 mg/L of orthophosphate-phosphorus. Concentrations greater than 0.20 mg/L must be diluted. The method was implemented in the National Water Quality Laboratory in March 1986 and modified in May 1989.

2. Summary of method

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966; Pai and others, 1990).

3. Interferences

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

3.2 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to phosphate (Murphy and Riley, 1962) and might cause a positive interference. Arsenic concentrations as much as 100 μg/L do not interfere. .

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge, heating bath, colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.001 to 0.20 mg/L phosphorus:

Flow cell	30 mm
Wavelength	880 nm
Sample time	24 seconds
Sampling rate	64 per hour
Wash time	32 seconds
Heating bath (2 mL)	37°C
Pecking	OFF
Damp (RC)	1 second

5. Reagents

5.1 *Ammonium molybdate solution,* 35.6 mg/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$ 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 $K(SbO)C_4H_4O_6\bullet 1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents in following order (this reagent is stable for about 8 h):

Sulfuric acid, 2.45M	100 mL
Ammonium molybdate solution	30 mL
Ascorbic acid solution	60 mL
Antimony potassium tartrate solution	10 mL

5.5 *Phosphorus 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.

5.6 *Phosphorus standard solution II*, 1.00 mL = 0.001 mg P: Dilute 10.0 mL phosphorus standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphorus working solutions:* Prepare a blank and *200* mL each of a series of working solutions by appropriate dilution of phosphorus standard solution II or working solution No. 3*,* as shown in the following table. If the samples to be analyzed are preserved, the phosphorus working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Phosphorus concentration (mg/L)
1	40	Standard solution II	0.200
2	20	Standard solution II	0.100
3	10	Standard solution II	0.050
4	2	Standard solution II	0.010
5	20	Working solution No. 3	0.005
6	8	Working solution No. 3	0.002
7	4	Working solution No. *3*	0.001

Prepare fresh weekly and refrigerate,

5.8 *Sodium lauryl sulfate solution,* 15 percent w/w: Dissolve 30 g sodium lauryl sulfate in 170 mL of demineralized water. Place flask in an ultrasonic bath to aid in dissolving sodium lauryl sulfate. **CAUTION**: Solid sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood.

5.9 *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. Cool, and dilute to 1,000 mL with demineralized water.

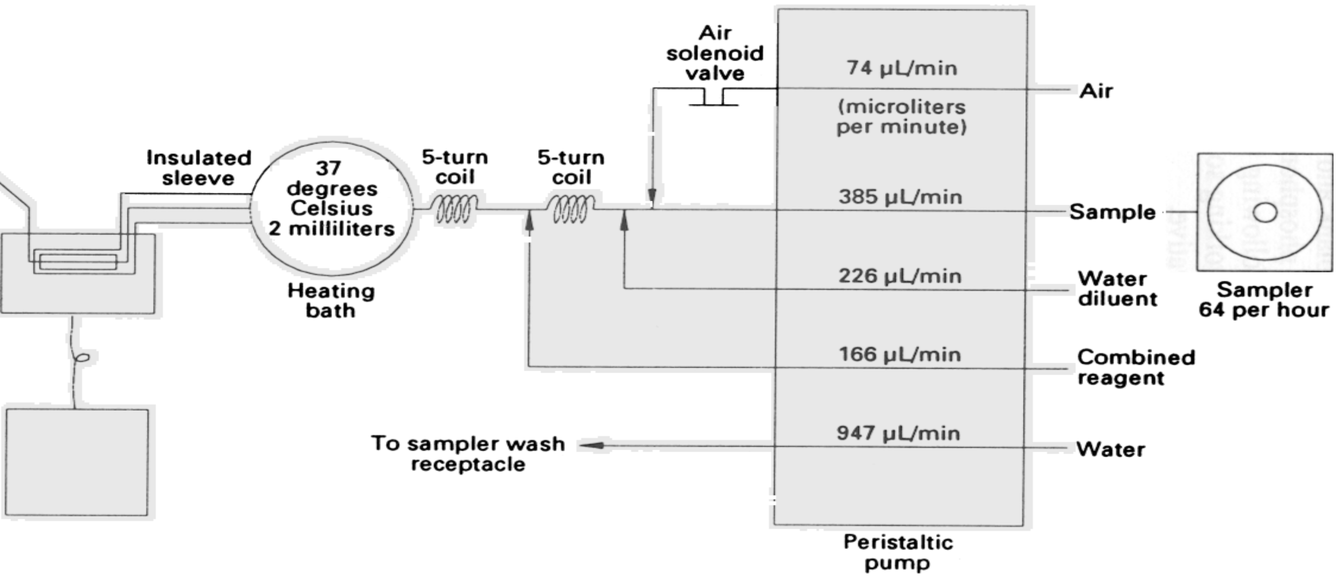
5.10 *Water diluent:* Dissolve 2.5 g NaCl in 400 mL demineralized water. Add 10 mL of sodium lauryl sulfate solution (paragraph 5.8*)* and dilute to 500 mL with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 1).

6.2 Allow colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath is 37°C.

6.3 After all reagents are on line, adjust the sample output of the photometer to *5 V.* Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).



1. - Phosphorus, orthophosphate, low ionic-strength water, phosphomolybdate manifold.

6.4 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.5 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.6 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in about every eighth position of the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.7 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve either by plotting the voltage of each working solution peak in relation to its respective orthophosphate-phosphorus concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved orthophosphate-phosphorus in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of phosphorus, orthophosphate, dissolved (00671), as follows: less than 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for dissolved orthophosphate-phosphorus, as determined for natural-water samples expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
22	0.160	0.001	6.2
22	0.189	0.003	1.6
22	0.196	0.002	1.0

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

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. 1363-1368.

Murphy, J., and Riley, J.P., 1962, A modified single-solution method for the determination of phosphorus in natural waters: Analytica Chimica Acta, v. 27, p. 31-36.

Pai, Su-Cheng, Yang, Chung-Cheng, and Riley, J.P., 1990, Effects of acidity and molybdate concentration on the kinetics of the formation of the phosphoantimonylmolybdenum blue complex: Analytica Chimica Acta, v. 229, p. 115-120.