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

Parameters and Codes:

Phosphorus, dissolved, I-2607-90 (mg/L as P): 00666
Phosphorus, total, I-4607-90 (mg/L as P): 00665

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 phosphorus. Concentrations greater than 0.20 mg/L must be diluted. This method was implemented in the National Water Quality Laboratory in March 1990.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus compounds, 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 reaction 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 phosphorus precipitate but the effect is negligible in natural water. The interference from silica, which forms a pale blue complex, is small and may be considered negligible. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chloride needs to be removed by boiling the sample.

3.2 Arsenic as arsenate (AsO_4^{-3}) produces a similar color as 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 *Autoclave.*

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

4.3 With this equipment, the following operating conditions are satisfactory for the range from 0.001 to 0.200 mg/L P:

Flow cell	30 mm
Wavelength	880 nm
Sample time	38 seconds
Sampling rate	60 per hour
Wash time	22 seconds
Heating bath (2 mL)	37°C
Pecking	OFF
Damp (RC)	4 seconds

4.4 *Glass tubes with plastic caps,* disposable, 16 x 150 mm.

5. Reagents

5.1 *Ammonium molybdate solution,* 35.6 g/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. Keep in 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 $K(SbO)C_4H_4O_6\bullet 1/2H_2O$ 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, 2.45*M*	100 mL
Ammonium molybdate solution	30 mL
Ascorbic acid solution	60 mL
Antimony potassium tartrate solution	10 mL

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

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

5.7 *Phosphorus standard solution II,* 1.00 mL = 0.001 mg P: Dilute 10 mL phosphorus standard solution I to 1,000 mL with demineralized water.

5.8 *Phosphorus working solutions:* Prepare a blank and 1,000 mL each of a series of working solutions by appropriate dilution of phosphorus standard solutions I and II, as listed 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	2	Standard solution I	0.200
2	1	Standard solution I	0.100
3	50	Standard solution II	0.050
4	10	Standard solution II	0.010
5	5	Standard solution II	0.005
6	1	Standard solution II	0.001

5.9 *Sulfuric acid solution,* 2.45*M:* Cautiously, add slowly, with constant stirring, 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1,000 mL with dernineralized water.

5.10 *Phosphorus catalyst:* Add slowly 25 mL concentrated sulfuric acid and 4.0 g potassium persulfate ($K_2S_2O_8$) to 1,800 mL demineralized water and dilute to 2 L.

5.11 *Water diluent:* Add 5 mL sodium lauryl sulfate solution to 250 mL demineralized water.

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.002 mg total phosphorus (10.0 mL maximum) into a disposable glass tube, and adjust volume to 10 mL.

6.2 Pipet 10 mL of blank and each of the working solutions into disposable glass tubes.

6.3 Add 4.0 mL phosphorus catalyst to each sample, working solution, and blank.

6.4 Place plastic caps on top of tubes. Autoclave for 30 minutes at 15 lb/in^2 pressure.

6.5 Set up manifold (fig. 1).

6.6 Allow colorimeter, recorder, and heating bath to warm up for at least 10 minutes or until the heating bath temperature reads 37°C.

6.7 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).

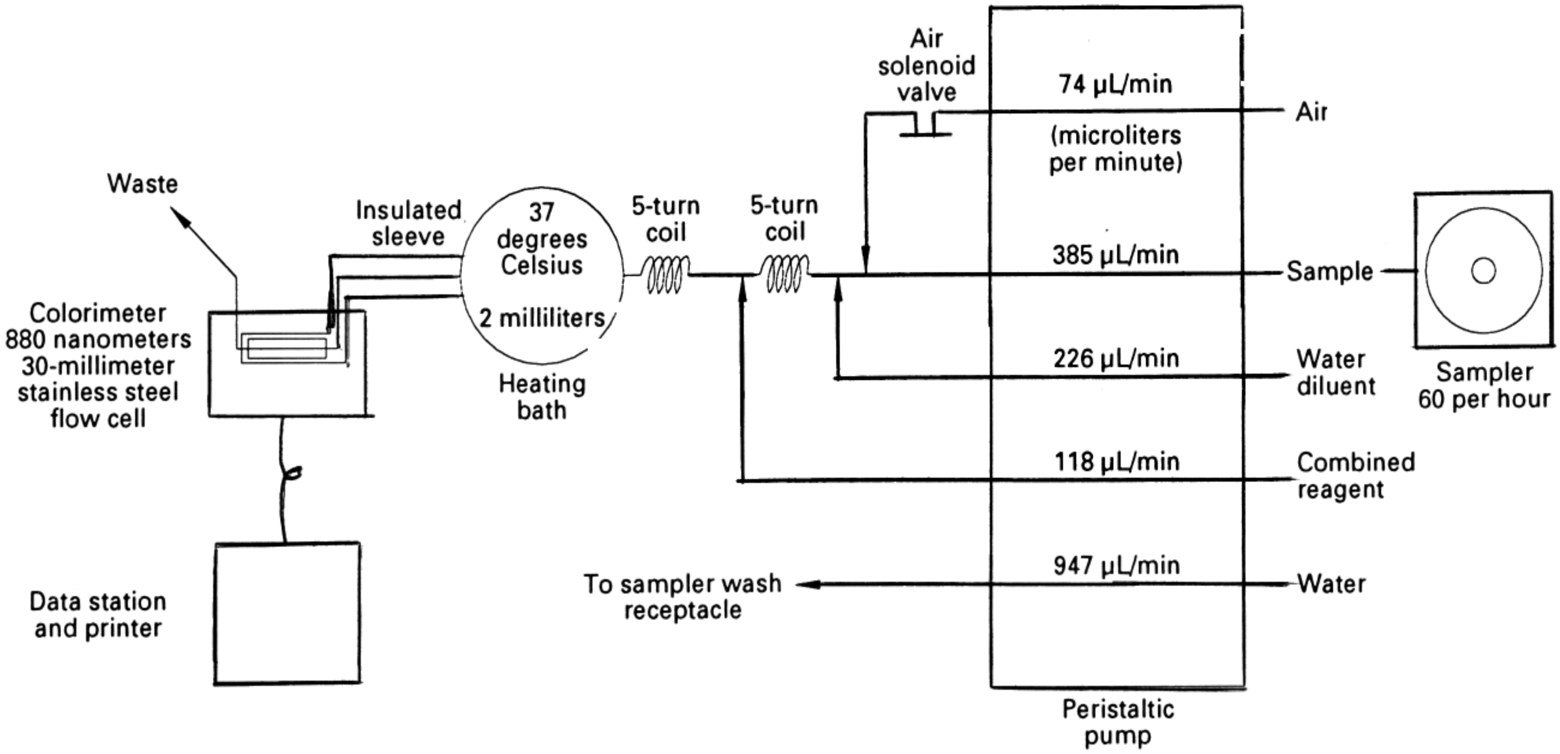
6.8 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.9 When the system has cleared of all working solutions, determine a dwell time using the most concentrated working solution.

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

6.11 Begin analysis.

Figure 1. - Phosphorous, low ionic-strength water, phosphomolybdate manifold.



7. Calculations

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

7.2 Compute the concentration of dissolved or total 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, dissolved (00666), or phosphorus, total (00665), 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 and total phosphorus, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
0.177	0.005	2.69
0.176	0.004	2.17
0.092	0.006	6.89
0.038	0.002	6.64
0.004	0.001	31.43

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 water: 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.