Phosphorus, colorimetry, phosphomolybdate, automated-segmented flow

Parameter and code:
Phosphorus, total-in-bottom-material, dry weight,
I-6600-88 (mg/kg as P): 00668

1. Application

This method is used to analyze samples of bottom material containing from 40 to 4,000 mg/kg of phosphorus. This modified method was implemented in the National Water Quality Laboratory in March 1988.

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 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 The color of the molybdate blue complex is strongly affected by pH.

3.2 Barium, lead, and silver interfere by forming a phosphorus precipitate but the effect is negligible. The interference from silica, which forms a pale-blue complex, is negligible. Residual chlorine needs to be removed by boiling the sample.

3.3 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. Greater concentrations were not investigated.

4. Apparatus

4.1 *Autoclave.*

4.2 *Glass tubes with plastic caps,* disposable 18x 150 mm.

4.3 *Technicon AutoAnalyzer II,* consisting of sampler, analytical cartridge, peristaltic pump, colorimeter, voltage stabilizer, data station, and printer.

4.4 With this equipment, the following operating conditions are satisfactory for the range from 0.01 to 1.0 mg/L phosphorus:

Absorption cell	50 mm
Wavelength	880 or 660 nm
Cam	40/h (5/1)
Heating-bath temperature	37°C

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 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 $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents in following order (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 *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 = 0.010 mg P: Dilute 100.0 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 quantitative dilution of phosphorus standard solution II as listed in the following table.

Working solution No.	Phosphorus standard solution II (mL)	Phosphorus concentration (mg/L)
1	1	0.05
2	2	.10
3	5	.25
4	10	.50
5	20	1.00

5.8 *Potassium persulfate,* crystals.

5.9 *Potassium persulfate solution,* 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

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

5.11 *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.

5.12 *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.

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

5.14 *Water diluent:* Dissolve 20 g NaCl in 800 mL demineralized water. Add 5.0 mL sodium lauryl sulfate solution and dilute to 1 L with demineralized water.

6. Procedure

6.1 Air dry an aliquot of thoroughly mixed bottom material at room temperature. (The sample needs to be sieved through a 2-mm plastic mesh sieve before air drying.)

6.2 Grind and sieve the air-dried sample through a 500-µm mesh sieve. Discard the portion retained on the sieve, and use for analysis only the portion that passed through the sieve. Run samples in duplicate. Samples need to agree within a relative percent difference of 20 percent (NOTE 1).

NOTE 1. Relative percentage difference = $\frac{\text{Absolute difference between duplicates}}{\text{Average of duplicates}} \times 100$

6.3 Weigh, to the nearest 0.0001 g, about 0.1 g of sample.

6.4 Transfer the samples to a 200-mL round bottom volumetric flask.

6.5 Add about 150 mL of demineralized water to each flask and place in an ultrasonic bath for 10 minutes.

6.6 Bring the flask to volume with demineralized water.

6.7 While stirring, pipet 5.0 mL of each sample into disposable glass tubes. Add 5.0 mL demineralized water. Prepare each sample in duplicate.

6.8 Pipet 10.0 mL of each working solution and a blank into disposable glass tubes.

6.9 Add 4.0 mL of sulfuric acid persulfate reagent.

7.0 Mix the sample and reagent thoroughly, using a vortex mixer.

7.1 Autoclave the samples for 30 minutes at 15 lb/in^2.

6.12 Allow the samples to cool.

6.13 Setup manifold (fig. 1).

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

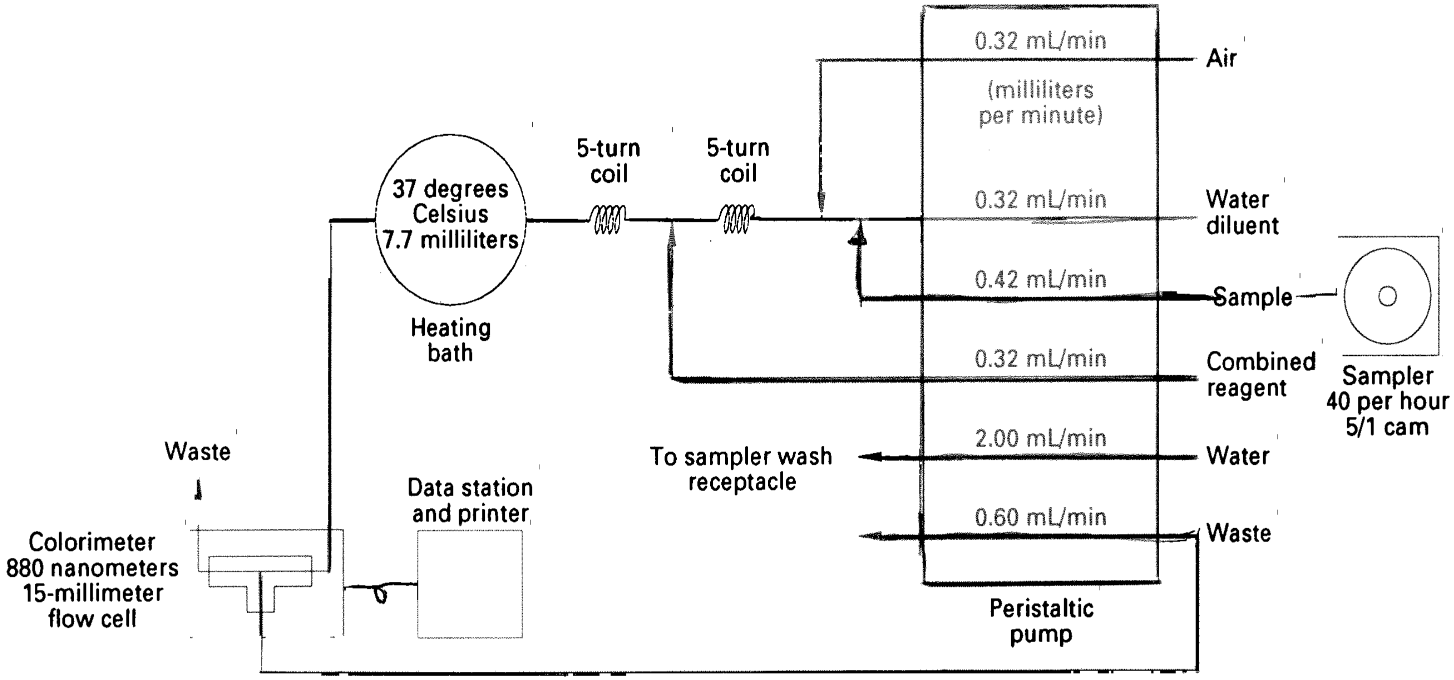

Figure 1.-Phosphorus, phosphomolybdate manifold.

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

6.16 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 remainder of this and subsequent sample trays. Fill the remainder of each tray with unknown samples.

6.17 Begin analysis. When the peak from the most concentrated working solution 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 working solution peak in relation to its respective phosphorus concentration or use a data reduction package. See operation manuals for complete details.

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

$$\text{Total phosphorus (mg/kg)} = \frac{P \times 0.01 \times 1{,}000 \times 40 \text{ (dilution factor)}}{W}$$

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

W = dry weight of sample, in grams.

8. Report

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

9. Precision

Typical precision for total phosphorus, expressed in standard deviation and percentage relative standard deviation, is as follows:

Number of laboratories	Mean (mg/kg)	Standard deviation (mg/kg)	Relative standard deviation (percent)
3	0.183	0.022	12
13	.572	.046	8
18	1.411	.127	9
15	3.59	.682	19

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. 1363-1368.

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.