Phosphorus, orthophosphate, colorimetric, phosphomolybdate, automated-discrete

Parameters and Codes:

Phosphorus, orthophosphate, dissolved, I-2598-85 (mg/L as P): 00671
Phosphorus, orthophosphate, total, I-4598-85 (mg/L as P): 70507

1. Application

1.1 This method may be used to analyze water, wastewater, brines, and water-suspended sediment containing from 0.01 to 2.0 mg/L orthophosphate-phosphorus. Samples containing concentrations greater than 2.0 mg/L need to be diluted.

1.2 To determine total orthophosphate-phosphorus, the suspended sediment in an unfiltered, unacidified sample is allowed to settle in the sample bottle and a portion of the clear supernatant solution is decanted for analysis.

2. Summary of method

2.1 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).

2.2 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 Because as phosphorus is easily adsorbed on sediment, the orthophosphate recovered from the supernatant solution above a water-suspended sediment after some time has elapsed may be less than the orthophosphate that would have been determined in the filtrate from a sample filtered at the time of collection. The amount recovered may also depend on the type of sediment (clay, sand, etc.).

3.2 Barium, lead, and silver interfere by forming a precipitate. 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.

3.3 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 up to 100 µg/L do not interfere. Greater concentrations were not investigated.

3.4 The blue color produced will coat the flow cell, causing a small but significant high bias. A 0.10-mg/L P spike is dispensed into the four leading wash tubes with the color reagent. The resulting blue color then coats the flow cell prior to the introduction of the working standards. By this action, the high bias is effectively eliminated.

4. Apparatus

4.1 *Discrete chemical analyzer system,* American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Wavelength --	880 nm
Absorption cell	1-cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature	37 °C
Sample volume	0.300 mL with 0.050 mL of diluent (NOTE 1)

Reagent volumes 0.25 mL color reagent
and 0.80 mL demineralized water (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

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 *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.

5.3 *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.

5.4 *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 *Phosphate standard solution I*, 1.00 mL = 1.00 mg P: Dissolve 4.394 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 *Phosphate standard solution II*, 1.00 mL = 0.05 mg P: Dilute 50.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate working standards*: Prepare a blank and 1,000 mL each of a series of phosphate working standards by appropriate quantitative dilution of phosphate standard solution II with demineralized water. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard. For example:

Standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
5.0	.25
10.0	.50
20.0	1.00
40.0	2.00

5.8 *Phosphate standard solution III (spike)*, 1.00 mL = 0.0001 mg P: Dilute 2.0 mL of phosphate standard solution II to 1,000 mL with demineralized water.

6. Procedure

6.1 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.3 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and the corresponding concentration calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total orthophosphate-phosphorus in each sample from either the CRT display or the printer output.

8. Report

Report phosphorus, orthophosphate, dissolved (00671), and total (70507), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.030	30	0.004	13.3
.152	30	.004	2.63
.737	24	.013	1.76
1.71	24	.009	.53
2.01	30	.017	.84