Phosphorus, orthophosphate, colorimetric, phosphomolybdate

Parameter and Code:
Phosphorus, orthophosphate, dissolved, I-1601-85 (mg/L as P): 00671

1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of orthophosphate-phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O$$
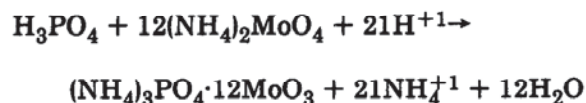
2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica produces a pale-blue color that is additive to the phosphate color, and may require correction. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined for each batch of reagents. 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. Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome this interference.

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

Spectrometer for use at 700 or 882 nm.

5. Reagents

5.1 *Antimony tartrate-ammonium molybdate solution*: Dissolve 0.13 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously*, add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.2 *Combined reagent solution*: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4 °C; otherwise prepare fresh daily.

5.3 *Phosphate standard solution I*, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4,

dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.4 *Phosphate standard solution II*, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 100-mL beaker, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 1).

NOTE 1. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 10 mL combined reagent solution to each sample, blank, and standard, and mix.

6.4 After 10, but before 30, min measure absorbance of each sample and standard against that of the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$P \ (mg/L) = \frac{1,000}{mL \ sample} \times mg \ P \ in \ sample$$

8. Report

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

9. Precision

9.1 Precision for dissolved orthophosphate-phosphorus for nine samples within the range of 0.000 to 1.70 mg/L may be expressed as follows:

$$S_T = 0.114 \, X + 0.004$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of orthophosphate-phosphorus, milligrams per liter.

The correlation coefficient is 0.9067.

9.2 Precision for dissolved orthophosphate-phosphorus for five of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.000	0
12	.008	62
15	.406	11
11	1.02	8
14	1.70	13

Reference

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.