



**Techniques of Water-Resources Investigations
of the United States Geological Survey**

Chapter A1

**METHODS FOR DETERMINATION
OF INORGANIC SUBSTANCES
IN WATER
AND FLUVIAL SEDIMENTS**

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Book 5
LABORATORY ANALYSIS

Oxygen demand, chemical (COD), colorimetric, dichromate oxidation

Parameter and Code:

Oxygen demand, chemical, total, 1-3561-85 (COD in mg/L): 00340

1. Application

This method may be used to analyze water-suspended sediment containing between 10 and 500 mg/L chemical oxygen demand (COD).

2. Summary of method

2.1 Organic and other oxidizable materials are oxidized by digestion with an acid-dichromate solution in the presence of silver sulfate catalyst. The COD concentration is determined spectrometrically by measuring the absorbance of the Cr^{+3} that is formed.

2.2 Additional information about the principles of the method may be found in Jirka and Carter (1975).

3. Interferences

3.1 Reducing substances such as ferrous iron and chloride interfere, because they are oxidized by dichromate in acid solution. Chlorides constitute the largest and most common interference, with 1 mg/L Cl^{-1} equivalent to 0.226 mg/L COD. To eliminate chloride interference as great as 2,000 mg/L, add mercuric sulfate to the acid-dichromate digestion solution.

3.2 Chromium(III) interferes. One milligram per liter is equivalent to 0.719 mg/L COD. Levels great enough to have significant effect on the accuracy are unlikely in natural water samples.

3.3 Ferric iron concentrations less than 5000 mg/L do not interfere.

4. Apparatus

4.1 *Ampules*, glass, 10-mL capacity.

4.2 *Centrifuge*, Sorvall SS-3 Automatic Superspeed or equivalent.

4.3 *Spectrometer* for use at 600 nm: Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Potassium acid phthalate standard solution I*, 1.0 mL = 10.0 mg COD: Dissolve 8.500 g potassium acid phthalate, which has been dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium acid phthalate standard solution II*, 1.0 mL = 1.0 mg COD: Dilute 100 mL potassium acid phthalate standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Potassium dichromate-mercuric sulfate digestion solution*: To approx 700 mL demineralized water, add 10.216 g $\text{K}_2\text{Cr}_2\text{O}_7$ and 33.0 g HgSO_4 . CAUTION: Hazardous. Slowly, and with constant stirring, add 167 mL concentrated H_2SO_4 (sp gr 1.84). Mix until dissolved. After the solution cools, dilute to 1 L with demineralized water.

5.4 *Silver sulfate solution*: Dissolve 22 g Ag_2SO_4 in a 9-pound bottle of concentrated H_2SO_4 (sp gr 1.84).

5.5 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Heat the ampules at 500°C for 6 h, and cool.

6.2 Pipet 2.5 mL of a well-mixed sample into an ampule.

6.3 Prepare a blank and sufficient standards containing from 10 to 500 mg/L COD using potassium acid phthalate standard solution II. Pipet 2.5 mL of each into ampules.

6.4 Add 1.5 mL potassium dichromate-mercuric sulfate digestion solution to each ampule (NOTE 1).

NOTE 1. Protective eyeglasses and clothing are mandatory for this entire procedure, because

sulfuric acid and potassium dichromate solutions at high temperatures are especially hazardous.

6.5 Add 3.5 mL silver sulfate solution to each ampule.

6.6 Heat-seal the ampules and shake vigorously.

6.7 Heat the ampules in an oven at 150°C for 2 h.

6.8 Cool the ampules to room temperature in a cold-water bath.

6.9 Centrifuge the solutions at 5,000 rpm for 15 min.

6.10 Set the spectrophotometer at 600 nm and adjust the absorbance to 0.000 with the digested blank.

6.11 Individually transfer each standard and sample to the sample cuvette, preferably using an automated flow-through cell, and read and record each absorbance value. Care must be taken not to disturb any precipitate when pouring the sample into the cuvette (NOTE 2).

NOTE 2. A Technicon AutoAnalyzer system, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, recorder, and printer, may be used in place of the spectrophotometer to measure the absorbance of the digested solution (Jirka and Carter, 1975). Steps 6.2 to 6.9 remain unchanged.

7. Calculations

Determine the milligrams per liter of COD in each sample from a plot of absorbances of standards.

8. Report

Report oxygen demand, chemical (COD), total (00340), concentrations as follows: less than 10 mg/L, as <10 mg/L; 10 mg/L and above, two significant figures.

9. Precision

For potassium acid phthalate standards, the precision for a single operator expressed in terms of the percent relative standard deviation is as follows:

Mean (mg/L)	Relative standard deviation (percent)
50	14
400	2

Reference

Jirka, A. M., and Carter, M. J., 1975, Micro semiautomated analysis of surface and wastewaters for chemical oxygen demand: *Analytical Chemistry*, v. 47, no. 8, p. 1397-1402.

Oxygen demand, chemical (COD), titrimetric, dichromate oxidation

Parameters and Codes:

Oxygen demand, chemical, total, 0.025N dichromate, I-3562-85 (COD in mg/L): 00335
Oxygen demand, chemical, total, 0.25N dichromate, I-3560-85 (COD in mg/L): 00340
Oxygen demand, chemical, total-in-bottom-materials, dry wt, I-5560-85 (COD in mg/kg): 00339

1. Application

1.1 This method may be used to analyze natural water and industrial waste containing more than 50 mg/L chemical oxygen demand (COD) and less than 2,000 mg/L of chloride. Samples containing less than 50 mg/L COD need to be analyzed as directed in paragraph 6.10. COD values for samples containing more than 2,000 mg/L of chloride need to be corrected as indicated in paragraph 6.11.

1.2 This method may be used to analyze samples of bottom material containing more than 100 mg/kg chemical oxygen demand (COD). Samples containing less than 1,000 mg/kg COD need to be analyzed as directed in paragraph 6.10.

1.3 Bottom material may be analyzed by the procedure after it has been prepared as directed in method P-0810 or P-0811.

2. Summary of method

2.1 Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator.

2.2 For additional information, see American Society for Testing and Materials, (1984).

3. Interferences

Reducing substances such as ferrous iron, nitrites, and chlorides interfere, because they are oxidized. Chlorides constitute by far the greatest and most common interference, being quantitatively oxidized by dichromate in acid solution. One milligram of chloride per liter is

equivalent to 0.226 mg/L COD. To eliminate chloride interference, add mercuric sulfate to the sample to form a soluble mercuric chloride complex. Nitrite interference may be eliminated by incorporating in the standard dichromate solution 10 mg of sulfamic acid for each milligram of nitrite in the reflux flask.

4. Apparatus

4.1 *Reflux apparatus*, consisting of 500-mL Erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hotplate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate standard solution I*, approx 0.250N: Dissolve 98.0 g $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in demineralized water. Add 20 mL concentrated H_2SO_4 (sp gr 1.84), cool, and dilute to 1 L with demineralized water. To standardize: Dilute 25.0 mL standard 0.2500N $\text{K}_2\text{Cr}_2\text{O}_7$ solution to 250 mL. Add 20 mL concentrated H_2SO_4 (sp gr 1.84) and cool. Titrate with the ferrous ammonium sulfate solution, using 8 to 10 drops ferroin indicator. Compute normality of the ferrous ammonium sulfate standard solution to four decimal places. The solution must be standardized daily or before use.

5.2 *Ferrous ammonium sulfate standard solution II*, 0.025N: Dilute 100 mL of ferrous ammonium sulfate standard solution I to 1,000 mL with demineralized water. The normality of this solution is dependent upon the standardized normality of solution I.

5.3 *Mercuric sulfate*, powdered HgSO_4 .

5.4 *Orthophenanthroline ferrous sulfate (ferroin) indicator solution*: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 mL water. The prepared indicator is available commercially.

5.5 *Potassium dichromate standard solution I, 0.2500N*: Dissolve 12.2588 g $\text{K}_2\text{Cr}_2\text{O}_7$ primary standard, dried for 2 h at 110°C , in demineralized water and dilute to 1,000 mL.

5.6 *Potassium dichromate standard solution II, 0.0250N*: Dilute 100 mL of potassium dichromate standard solution I to 1,000 mL with demineralized water.

5.7 *Silver sulfate, powder, Ag_2SO_4* .

5.8 *Sulfamic acid, crystals*.

5.9 *Sulfuric acid, concentrated (sp gr 1.84)*.

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for natural waters and industrial wastes, and in paragraph 6.1.2 for bottom materials.

6.1.1 Pipet 50.0 mL of a well-mixed sample or of a smaller volume diluted to 50.0 mL into the reflux flask.

6.1.2 Weigh, to the nearest milligram, an amount of wet sample (1.0 g max) that will consume approx one-half of the 0.2500N $\text{K}_2\text{Cr}_2\text{O}_7$ solution added in paragraph 6.5. Transfer the sample to the reflux flask and add 50 mL demineralized water.

6.2 Add slowly, over a period of 2 to 3 min, 1 g HgSO_4 ; allow to stand 5 min, swirling frequently.

6.3 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 h.

6.4 Cool in ice water and add 75 mL concentrated H_2SO_4 (sp gr 1.84) slowly enough, with mixing, to prevent appreciable solution heating.

6.5 Add 25.0 mL 0.2500N $\text{K}_2\text{Cr}_2\text{O}_7$ solution and mix thoroughly by swirling (NOTE 1).

NOTE 1. If contents are not well mixed, superheating may result, and the contents of the flask may be expelled from the open end of the condenser.

6.6 Attach flask to condenser, start water flow, and reflux for 2 h.

6.7 Allow flask to cool and wash condenser with 25 mL demineralized water.

6.8 Dilute to 300 mL with demineralized water, cool to room temperature, and titrate the excess dichromate with ferrous ammonium

sulfate standard solution I, using 8 to 10 drops ferroin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.9 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.10 Samples containing less than 50 mg/L COD or 1,000 mg/kg COD should be reanalyzed, using 0.025N solutions of potassium dichromate and ferrous ammonium sulfate. A sample size should be selected so that no more than half the dichromate is reduced.

6.11 To determine COD on samples containing more than 2,000 mg/L of chloride, the following treatment should be used (Burns and Marshall, 1965). Add 10 mg HgSO_4 for each milligram of chloride ion in the sample aliquot. Prepare a series of chloride solutions containing from 2,000 to 20,000 mg/L with the concentration interval not exceeding 4,000 mg/L, and add 10 mg HgSO_4 to each solution for each milligram of chloride ion present. Determine the COD of the sample and chloride solution, starting with paragraph 6.2. Plot the COD values obtained versus milligrams per liter chloride. From this curve, COD values may be obtained for any desired chloride concentration. This value is subtracted as a correction factor to obtain the COD value of a sample.

7. Calculations

7.1 For natural waters and industrial wastes not requiring chloride correction:

$$\text{COD (mg/L)} = \frac{(A-B)N \times 8,000}{\text{mL sample}}$$

7.2 For natural waters and industrial wastes requiring chloride correction:

$$\text{COD (mg/L)} = \left[\frac{(A-B)N \times 8,000}{\text{mL sample}} - C \right] \times 1.20$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

N = normality ferrous ammonium sulfate,

C = chloride-correction value from graph of chloride concentration versus COD,

and

1.20 = empirical compensation factor.

7.3 Compute the dry weight of the bottom-material samples as follows:

$$\text{Sample, dry weight (g)} = W \frac{(100-M)}{100}$$

where

W = wet weight of the sample, grams,

and

M = percentage moisture.

7.4 Determine the chemical oxygen demand in each bottom-material sample as follows (NOTE 2):

NOTE 2. Most bottom-material samples contain low concentrations of chloride; therefore, a chloride correction is not necessary.

$$\text{COD (mg/kg)} = \frac{(A-B)N \times 8,000}{\text{sample, dry weight (g)}}$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

and

N = normality ferrous ammonium sulfate.

8. Report

8.1 Report COD, total, 0.025*N* dichromate (00335), as follows: less than 50 mg/L, whole numbers.

8.2 Report COD, total, 0.25*N* dichromate (00340), as follows: 50 mg/L and above, two significant figures.

8.3 Report COD, total-in-bottom-material, dry-weight (00339), as follows: less than 10,000 mg/kg, to the nearest 100 mg/kg; 10,000 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

- American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 62-8.
- Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Journal, v. 37, p. 1716-21.

pH, electrometric, glass-electrode

Parameters and Codes:

pH lab, I-1586-85 (units): 00403

pH lab, automated, I-2587-85 (units): 00403

1. Application

This method may be used to determine the pH of any natural or treated water and any industrial or other wastewater.

2. Summary of method

2.1 See the introduction to electrometry in this chapter for the principles of pH-meter operation. See also Barnes (1964), Bates (1964), and Willard and others (1965).

2.2 This procedure may be automated with commercially available instrumentation.

3. Interferences

3.1 The determination is not affected by the presence of color or turbidity, or of organic or colloidal material. Oxidizing and reducing substances do not impair the accuracy of method.

3.2 The pH measurement is temperature dependent, and a significant error results if the temperatures of the buffers and samples differ appreciably. However, a variation of less than 5°C has no significant effect except in the most exacting work.

3.3 For samples having abnormally high sodium levels, corrections may be necessary. This correction varies with the type of electrodes used; hence, see the manufacturer's instructions for the necessary computations.

4. Apparatus

4.1 *pH meter*, with glass and reference electrodes or combination pH electrode.

4.2 Several types of pH meters are available, including digital and expanded-scale models. Unless a different type is needed for special purposes, an ordinary laboratory, line-operated, pH meter—capable of a reproducibility of 0.05 of a pH unit—is adequate.

4.3 A new glass electrode or one that has dried completely may require several hours of soaking in water or buffer solution before it produces stable, reliable readings. The tip of the glass electrode must be kept immersed in water when not in use. Although the glass tip is reasonably durable, it can be damaged, and should never be cleaned or wiped with an abrasive or dirty tissue or cloth.

5. Reagents

Standard buffer solutions, pH 4.00, 7.00, and 9.00: These buffers should cover the range of pH of the samples to be measured. If samples of pH less than 4.00 or greater than 9.00 are to be analyzed, additional buffers will be required. Ready-made buffer reagents are satisfactory.

6. Procedure

6.1 After an appropriate warmup period, standardize the instrument with the buffer solutions, bracketing the pH values of the samples. Samples and buffers must be at the same temperature.

6.2 With a minimum of aeration or agitation, measure the pH of samples in accordance with the manufacturer's instructions.

7. Calculations

The pH is read directly from the meter.

8. Report

Report pH values (00403) to the nearest 0.1 pH unit.

9. Precision

9.1 Precision for pH for five of the 36 samples expressed in terms of standard deviation is as follows:

<u>Number of laboratories</u>	<u>Mean (pH units)</u>	<u>Relative standard deviation (pH units)</u>
27	6.21	0.26
59	7.14	.32
33	7.52	.15
48	8.00	.21
60	8.54	.15

9.2 Using automated instrumentation, analysis of two test samples by a single laboratory for 25 replicates of each resulted in mean values of 7.58 and 8.07 pH units and standard

deviations of 0.05 and 0.03 pH units, respectively.

References

- Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water Supply Paper 1535-H, 17 p.
- Bates, R. G., 1964, Determination of pH—theory and practice: New York, John Wiley and Sons, 435 p.
- Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1974, Instrumental methods of analysis (5th ed.): New York, D. Van Nostrand, 860 p.

Phosphorus, colorimetric, phosphomolybdate

Parameter and Code:

Phosphorus, dissolved, I-1600-85 (mg/L as P): 00666

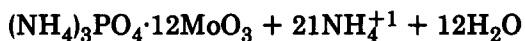
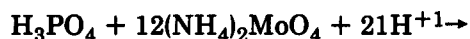
1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of dissolved 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 polyphosphate, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable and organic forms of phosphorus are decomposed to orthophosphate by sulfuric acid-ammonium persulfate digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:



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 up to 100 $\mu\text{g/L}$ do not interfere. Greater concentrations were not investigated.

4. Apparatus

Spectrometer for use at 700 or 882 nm.

5. Reagents

5.1 *Ammonium persulfate*, $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

5.2 *Antimony tartrate-ammonium molybdate solution*: Dissolve 0.13 g antimony potassium tartrate, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 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.

5.3 *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.

5.4 *Phenolphthalein indicator solution*, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.5 *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.

5.6 *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.

5.7 *Sodium hydroxide, 3M*: Carefully, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.8 *Sulfuric acid, 6M*: Cautiously, add slowly, with constant stirring and cooling, 330 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.9 *Sulfuric acid, 0.25M*: Cautiously, add slowly, with constant stirring and cooling, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 125-mL Erlenmeyer flask, 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 1.0 mL 6M H_2SO_4 and 0.4 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3M NaOH, and then carefully add 0.25M H_2SO_4 until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

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

6.6 After 10 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:

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

8. Report

Report phosphorus, dissolved (00666), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved phosphorus within the range of 0.138 to 3.14 mg/L for 21 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.272 mg/L ranged from 0.252 to 0.296 mg/L.

9.2 Precision for dissolved phosphorus for six of the 21 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
13	0.138	48
15	.573	27
14	.867	5
16	.887	49
18	1.52	30
15	3.20	5

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.

Phosphorus, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, dissolved, I-2600-85 (mg/L as P): 00666

Phosphorus, total, I-4600-85 (mg/L as P): 00665

Phosphorus, total-in-bottom-material, dry wt, I-6600-85 (mg/kg as P): 00668

1. Application

1.1 This method may be used to analyze most water, wastewater, brines, and water-suspended sediment containing from 0.01 to 1.0 mg/L of phosphorus. Samples containing greater concentrations need to be diluted.

1.2 This method may be used to analyze bottom material containing from 40 to 4,000 mg/kg of phosphorus. This range may be extended by using a 0.1-g subsample rather than the 1-g subsample specified.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, 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 colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966).

2.3 Mercuric chloride-preserved water samples and water-suspended sediment mixtures are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

2.4 Digested and centrifuged bottom-material samples are diluted to reduce the acid and phosphorus concentrations before final analysis.

3. Interferences

3.1 The color of the molybdate blue complex is strongly affected by pH. The method incorporates a dilution step for bottom-material

samples to reduce the hydrogen-ion concentrations of all samples.

3.2 Barium, lead, and silver interfere by forming a phosphate precipitate, but the effect is usually negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small 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 as much as 100 $\mu\text{g/L}$ do not interfere. Greater concentrations were not investigated.

4. Apparatus

4.1 *Autoclave.*

4.2 *Centrifuge.*

4.3 *Centrifuge tubes, 50-mL capacity.*

4.4 *Glass tubes with plastic caps, disposable, 18×150 mm.*

4.5 *Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.*

4.6 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L P:

Absorption cell	-----	50 mm
Wavelength	-----	880 nm or 660 nm
Cam	-----	40/h (5/1)
Heating-bath temperature	-----	37.5°C

5. Reagents

5.1 *Ammonium molybdate solution*, 35.6 g/L: Dissolve 40 g ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid solution*, 18 g/L: Dissolve 18 g ascorbic acid $(\text{C}_6\text{H}_8\text{O}_6)$ 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 $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot\frac{1}{2}\text{H}_2\text{O}$ 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, 2.45M - 50 mL

Ammonium molybdate

solution ----- 15 mL

Ascorbic acid solution 30 mL

Antimony potassium

tartrate solution -- 5 mL

5.5 *Levor V solution* or equivalent.

5.6 *Phosphate 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.

5.7 *Phosphate standard solution II*, 1.00 mL = 0.010 mg P: Dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 *Phosphate working standards*: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II with demineralized water. Dissolve 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
5.0	.25
10	.50
20	1.00

5.9 *Potassium persulfate*, crystals.

5.10 *Potassium persulfate solution*, 4 g/L: Dissolve 4.0 g $\text{K}_2\text{S}_2\text{O}_8$ in demineralized water and dilute to 1 L.

5.11 *Sulfuric acid*, concentrated (sp gr 1.84).

5.12 *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 and dilute to 1 L with demineralized water.

5.13 *Sulfuric acid*, 0.45M: *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.

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

5.15 *Water diluent*: Dissolve 20g NaCl in 800 mL demineralized water. Add 2.0 mL Levor V and dilute to 1L with demineralized water.

6. Procedure

6.1 Follow instructions in paragraphs 6.1.1 through 6.1.4 for water or water-suspended sediment and in paragraphs 6.1.5 through 6.1.12 for bottom material.

6.1.1 Pipet a volume of well-mixed sample containing less than 0.01 mg total P (10.0 mL max) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.1.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

6.1.3 Add 4.0 mL sulfuric acid-persulfate reagent.

6.1.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter those samples containing sediment through a 0.45- μm membrane filter. Proceed to paragraph 6.2.

6.1.5 Accurately weigh a portion of as-received sample having a dry weight of approx 1 g. The sample must first be prepared as directed in method P-0810. Transfer the weighed sample to a 50-mL centrifuge tube and add 10 mL demineralized water.

6.1.6 On a separate portion, determine the dry weight of the sample (method P-0590).

6.1.7 Add 1.0 mL concentrated H_2SO_4 and 1.0 g potassium persulfate to each centrifuge tube.

6.1.8 Autoclave for 30 min at 15 psi pressure.

6.1.9 Centrifuge for 5 to 10 min at 5,000 rpm.

6.1.10 Transfer the supernatant solution to a 200-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.11 Wash the residue several times with demineralized water, adding the washings to the volumetric flask. Dilute to 200 mL with demineralized water.

6.1.12 Pipet 5.0 mL of sample, into a 100-mL volumetric flask and dilute to volume with demineralized water. Proceed to paragraph 6.2 (NOTE 1).

NOTE 1. Use blank and standards as prepared in paragraphs 6.1.2 through 6.1.4.

6.2 Set up manifold (fig. 37).

6.3 Allow colorimeter, recorder, and heating bath to warm for at least 30 min or until the temperature of the heating bath is 37.5°C.

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

6.5 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and

subsequent sample trays. Fill remainder of each tray with unknown samples.

6.6 Begin analysis. When the peak from the most concentrated standard 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 standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of dissolved or total phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

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

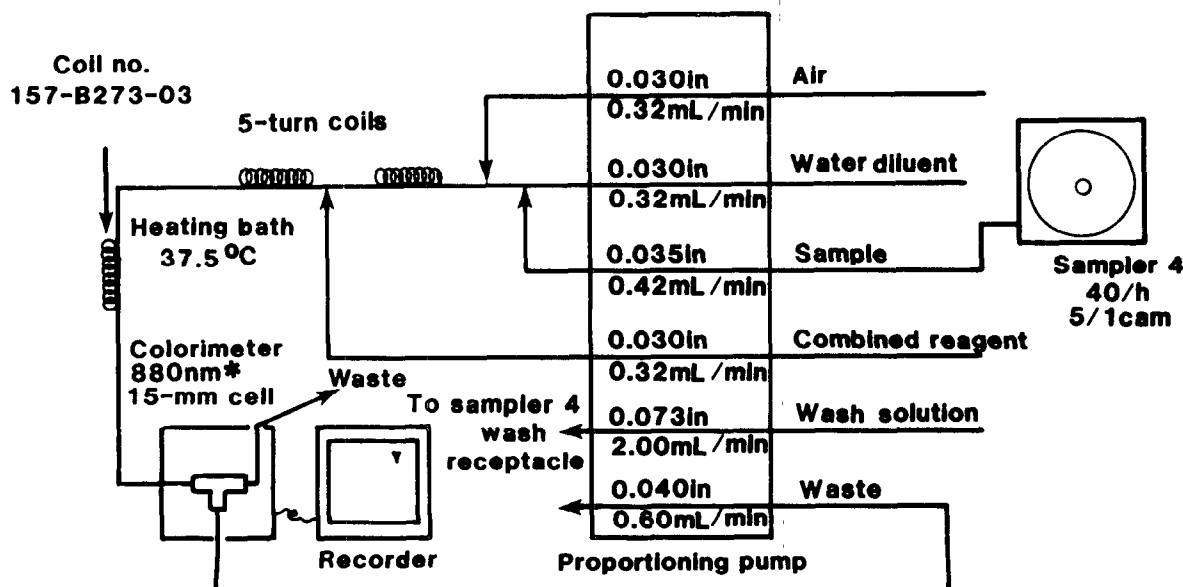
$$\text{Phosphorus (mg/kg)} = \frac{P}{5} \times \frac{20}{W} \times 1,000$$

where

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

and

W = dry weight, grams, of the sample.



* Alternatively 660 nm

Figure 37.—Phosphorus, phosphomolybdate manifold

8. Report

8.1 Report phosphorus, dissolved (00666), and total (00665), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

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

9. Precision

9.1 Precision for dissolved phosphorus for 20 samples within the range of 0.183 to 3.59 mg/L may be expressed as follows:

$$S_T = 0.189 X - 0.062$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of phosphorus, milligrams per liter.

The correlation coefficient is 0.9260.

9.2 Precision for dissolved phosphorus for four of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.183	12
13	.572	8
18	1.411	9
15	3.59	19

9.3 It is estimated that the percent relative standard deviation for total phosphorus and for total phosphorus in bottom material will be greater than that reported for dissolved phosphorus.

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. 1363-8.
- 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.

Phosphorus, colorimetric, phosphomolybdate, automated-discrete

Parameters and Codes:

Phosphorus, dissolved, I-2599-85 (mg/L as P): 00666

Phosphorus, total, I-4599-85 (mg/L as P): 00665

1. Application

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

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, 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 colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966).

2.3 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 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.

3.2 Arsenic as arsenate (AsO_4^{3-}) produces a color similar to that of (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 $\mu\text{g/L}$ do not interfere. Greater concentrations were not investigated.

3.3 The blue color produced will coat the flow cell, causing a small but significant high bias.

A 0.1-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	0.400 mL with 0.050 mL 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.

4.3 *Autoclave*.

4.4 *Glass tubes with plastic caps*, disposable, 18 by 150 mm.

5. Reagents

5.1 *Ammonium molybdate solution*, 35.6 g/L: Dissolve 40 g ammonium molybdate,

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 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, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot\frac{1}{2}\text{H}_2\text{O}$, in 800 mL demineralized water and dilute to 1 L.

5.3 *Ascorbic acid solution*, 18 g/L: Dissolve 18 g ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) 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, 2.45M	-----	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 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 phosphate standard solution II to 1,000 mL with demineralized water.

5.9 *Potassium persulfate solution*, 4 g/L: Dissolve 4.0 g $\text{K}_2\text{S}_2\text{O}_8$ in demineralized water and dilute to 1 L.

5.10 *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 and dilute to 1 L with demineralized water.

5.11 *Sulfuric acid, 0.45M*: 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.

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

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.02 mg total P (10.0 mL max) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

6.3 Add 4.0 mL sulfuric acid-persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter those samples containing sediment through a 0.45- μm membrane filter.

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

6.6 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.

6.7 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and the corresponding concentrations 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 phosphorus in each sample from either the CRT display or the printer output.

8. Report

Report phosphorus, dissolved (00666), and total (00665), 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)
0.142	27	0.009	6.34
.551	25	.009	1.63
.750	25	.009	1.20
1.00	25	.015	1.50
1.72	22	.007	.41
2.00	25	.027	1.35

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. 1363-8.
- 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.

Phosphorus, orthophosphate plus hydrolyzable, colorimetric, phosphomolybdate

Parameter and Code:

Phosphorus, orthophosphate plus hydrolyzable, dissolved, I-1602-85 (mg/L as P): 00677

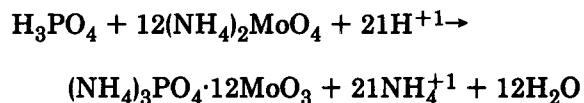
1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of dissolved orthophosphate plus hydrolyzable 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 Acid hydrolyzable phosphorus is decomposed to orthophosphate by sulfuric acid digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:



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 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 gives 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 $\mu\text{g/L}$ 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, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 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 *Phenolphthalein indicator solution*, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.4 *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.

5.5 *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.

5.6 *Sodium hydroxide*, 3M: Carefully, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sulfuric acid*, 6M: Cautiously, add slowly, with constant stirring and cooling, 330 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 0.25M: Cautiously, add slowly, with constant stirring and cooling, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 125-mL Erlenmeyer flask, 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 1.0 mL 6M H_2SO_4 . Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3M NaOH,

and then carefully add 0.25M H_2SO_4 until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

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

6.6 After 10 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:

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

8. Report

Report phosphorus, orthophosphate plus hydrolyzable, dissolved (00677), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for dissolved orthophosphate plus hydrolyzable phosphorus will be equal to that reported for dissolved phosphorus.

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.

Phosphorus, orthophosphate plus hydrolyzable, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, orthophosphate plus hydrolyzable, dissolved, I-2602-85 (mg/L as P): 00677

Phosphorus, orthophosphate plus hydrolyzable, total, I-4602-85 (mg/L as P): 00678

1. Application

This method may be used to analyze most water, brines, and water-suspended sediment containing between 0.01 and 1.0 mg/L combined acid hydrolyzable and orthophosphate-phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 Polyphosphates (P_2O_7)⁻⁴, (P_3O_{10})⁻⁵, etc., and a few organic phosphorus compounds are converted to orthophosphate by an acid hydrolysis.

2.2 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).

2.3 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 Barium, lead, and silver interfere by forming a phosphate precipitate, but the effect is usually negligible in natural waters. 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.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

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 μ g/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L combined hydrolyzable and orthophosphate-phosphorus:

Absorption cell	-----	50 mm
Wavelength	-----	880 nm or 660 nm
Cam	-----	40/h (5/1)
Heating-bath temperature	-----	37.5°C

4.4 *Glass tubes with plastic caps*, disposable, 18 × 150 mm.

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 *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, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, 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, 2.45M -----	50 mL
Ammonium molybdate solution -----	15 mL
Ascorbic acid solution ----	30 mL
Antimony potassium tartrate solution -----	5 mL

5.5 *Levor V solution* or equivalent.

5.6 *Phosphate 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.

5.7 *Phosphate standard solution II*, 1.00 mL = 0.010 mg P: Dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 *Phosphate working standards*: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. Dissolve 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
5.0	.25
10	.50
20	1.00

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 and dilute to 1 L with demineralized water.

5.10 *Sulfuric acid, 0.45M*: *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.

5.11 *Water diluent*: Dissolve 20 g NaCl in 800 mL demineralized water. Add 2.0 mL Levor V and dilute to 1 L with demineralized water.

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.01 mg combined hydrolyzable and orthophosphate-phosphorus (10.0 mL max) into a disposable glass tube and adjust the volume to 10.0 mL.

6.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

6.3 Add 2.0 mL 0.45M sulfuric acid.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter those samples containing sediment through a 0.45- μ m membrane filter.

6.5 Set up manifold (fig. 38).

6.6 Allow colorimeter, recorder, and heating bath to warm for at least 30 min or until the temperature of the heating bath is 37.5°C.

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

6.8 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

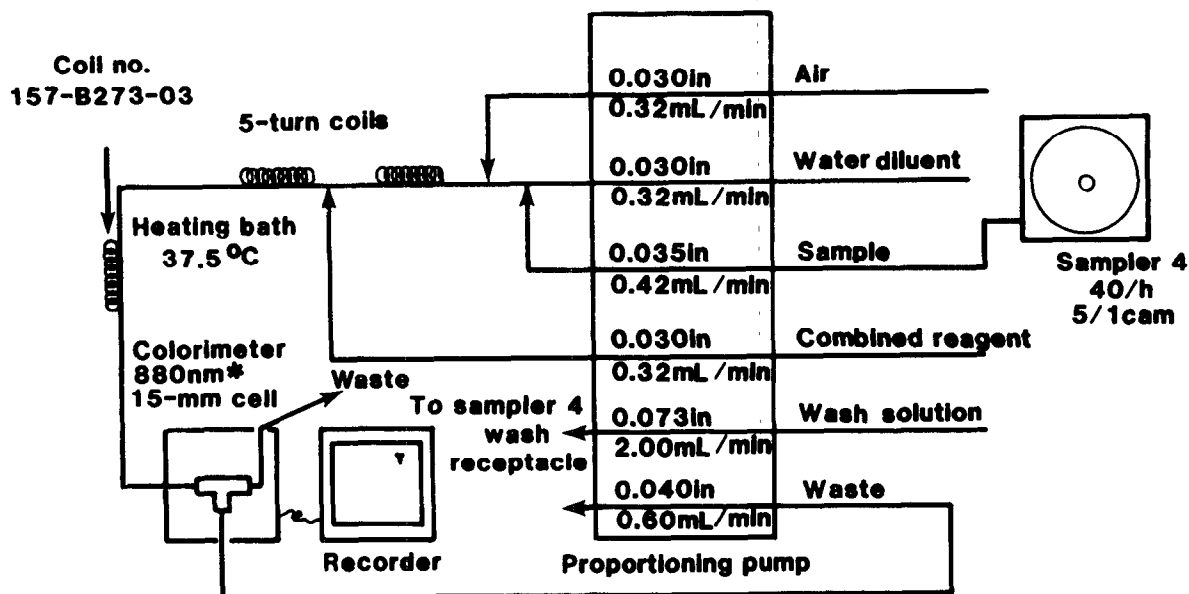
7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of dissolved or total phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report phosphorus, orthophosphate plus hydrolyzable, dissolved (00677), and total (00678), concentrations as follows: less than 1



* Alternatively 660 nm

Figure 38.—Phosphorus, phosphomolybdate manifold

mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for dissolved and total orthophosphate plus hydrolyzable phosphorus will be equal to that reported for phosphorus by the automated phosphomolybdate method.

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. 1363-8.
- 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.

Phosphorus, orthophosphate, colorimetric, phosphomolybdate

Parameter and Code:

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

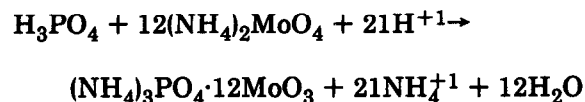
1. Application

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:



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 $\mu\text{g/L}$ 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, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 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:

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

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.

Phosphorus, orthophosphate, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, orthophosphate, dissolved, I-2601-85 (mg/L as P): 00671
Phosphorus, orthophosphate, total, I-4601-85 (mg/L as P): 70507

1. Application

1.1 This method may be used to analyze most water, wastewater, brines, and water-suspended sediment containing between 0.01 and 1.0 mg/L orthophosphate-phosphorus.

1.2 Total orthophosphate-phosphorus is determined by allowing the suspended sediment in an unfiltered, unacidified sample to settle in the sample bottle and by decanting a portion of the clear supernatant solution 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 phosphate precipitate, but the effect is usually negligible in natural waters. 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 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.4 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 $\mu\text{g/L}$ do not interfere. Greater concentrations were not investigated.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L P:

Absorption cell	-----	50 mm
Wavelength	-----	880 nm or 660 nm
Cam	-----	40/h (5/1)
Heating bath	-----	37.5°C

5. Reagents

5.1 *Ammonium molybdate solution*, 35.6 g/L: Dissolve 40 g ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid solution*, 18 g/L: Dissolve 18 g ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) 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, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order and volumes listed below. This reagent is stable for about 8 hr:

Sulfuric acid, 2.45M	-----	50 mL
Ammonium molybdate solution	-----	15 mL
Ascorbic acid solution	----	30 mL
Antimony potassium tartrate solution	-----	5 mL

5.5 *Levor V solution* or equivalent.

5.6 *Phosphate 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.

5.7 *Phosphate standard solution II, 1.00 mL = 0.010 mg P:* Dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 *Phosphate working standards:* Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. Dissolve 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
5.0	.25
10	.50
20	1.00

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 L with demineralized water.

5.10 *Water diluent:* Dissolve 20 g NaCl in 800 mL demineralized water. Add 2.0 mL Levor V and dilute to 1 L with demineralized water.

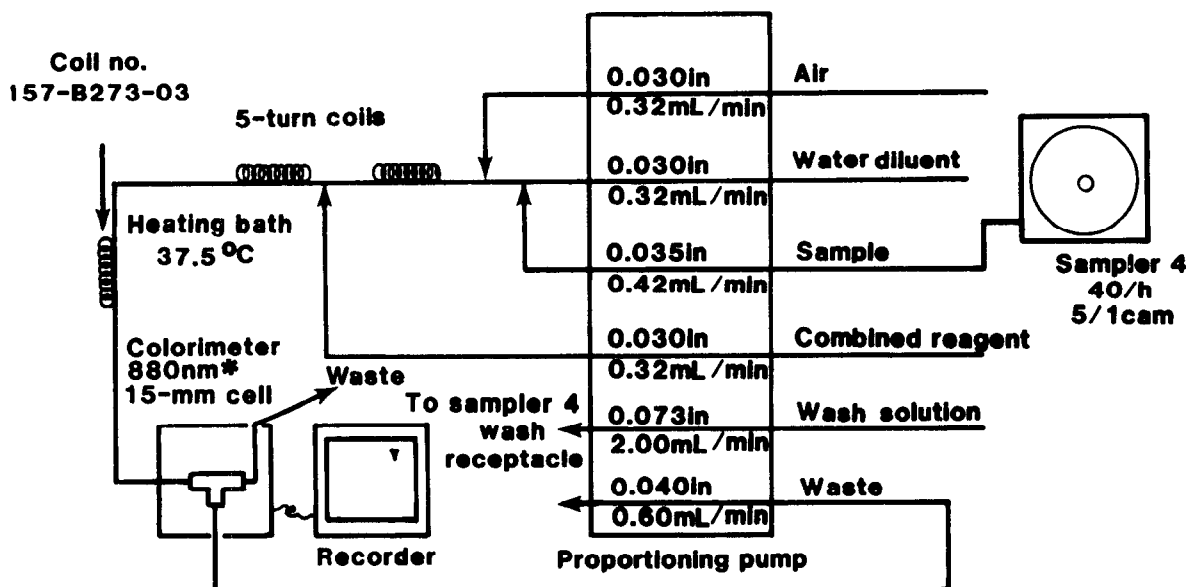
6. Procedure

6.1 Set up manifold (fig. 39).

6.2 Allow colorimeter, recorder, and heating bath to warm for at least 30 min or until the temperature of the heating bath is 37.5°C.

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

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing



* Alternatively 660 nm

Figure 39.—Phosphorus, phosphomolybdate manifold

concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples (NOTE 1).

NOTE 1. For water-suspended sediment, decant a portion of the clear supernatant solution from a settled sample for analysis. Avoid transfer of any particulate matter to the sample cups.

6.5 Begin analysis. When the peak from the most concentrated standard 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 standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of dissolved or total orthophosphate-phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report phosphorus, orthophosphate, dissolved (00671), and total (70507), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved orthophosphate-phosphorus for 9 samples within the

range of 0.007 to 1.93 mg/L may be expressed as follows:

$$S_T = 0.106X + 0.015$$

where

S_T = overall precision, milligrams per liter, and

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

The correlation coefficient is 0.8580.

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

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.007	86
20	.404	11
18	1.07	10
17	1.93	13

9.3 It is estimated that the percent relative standard deviation for total orthophosphate-phosphorus will be equal to or greater than that reported for dissolved orthophosphate-phosphorus.

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. 1363-8.
- 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.

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 $\mu\text{g/L}$ 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, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 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, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot \frac{1}{2}\text{H}_2\text{O}$, in 800 mL demineralized water and dilute to 1 L.

5.3 *Ascorbic acid solution*, 18 g/L: Dissolve 18 g ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) 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, 2.45M -----	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

Phosphorus, orthophosphate, ion-exchange chromatographic, automated

Parameters and Codes:

Phosphorus, orthophosphate, dissolved, I-2057-85 (mg/L as P): 00671

Phosphorus, orthophosphate, dissolved, I-2058-85 (mg/L as P): 00671

2. Summary of method

Orthophosphate is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The

separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and I-2058, anions, ion-exchange chromatographic, precipitation, automated.

Phosphorus, hydrolyzable and organic, calculation

Parameters and Codes:

Phosphorus, hydrolyzable, dissolved (mg/L as P): 00672
Phosphorus, hydrolyzable, total (mg/L as P): 00669
Phosphorus, organic, dissolved (mg/L as P): 00673
Phosphorus, organic, total (mg/L as P): 00670

1. Application

This method may be used to calculate dissolved and total hydrolyzable phosphorus, and dissolved and total organic phosphorus, on which the following parameters have been determined:

Parameters	Method No.
Phosphorus, orthophosphate, dissolved	I-1601 or I-2601 or I-2598
Phosphorus, orthophosphate, total	I-4601 or I-4598
Phosphorus, orthophosphate plus hydrolyzable, dissolved	I-1602 or I-2602
Phosphorus, orthophosphate plus hydrolyzable, total	I-4602
Phosphorus, dissolved	I-1600 or I-2600 or I-2599
Phosphorus, total	I-4600 or I-4599

2. Summary of method

Dissolved or total hydrolyzable phosphorus is determined by subtracting dissolved or total orthophosphate-phosphorus from dissolved or total orthophosphate plus hydrolyzable phosphorus, respectively. Dissolved or total organic phosphorus is determined by subtracting dissolved or total orthophosphate plus

hydrolyzable phosphorus from dissolved or total phosphorus, respectively.

7. Calculations

7.1 Phosphorus, hydrolyzable, dissolved (mg/L) = phosphorus, orthophosphate plus hydrolyzable, dissolved (mg/L) — phosphorus, orthophosphate, dissolved (mg/L).

7.2 Phosphorus, hydrolyzable, total (mg/L) = phosphorus, orthophosphate plus hydrolyzable, total (mg/L) — phosphorus, orthophosphate, total (mg/L).

7.3 Phosphorus, organic, dissolved (mg/L) = phosphorus, dissolved (mg/L) — phosphorus, orthophosphate plus hydrolyzable, dissolved (mg/L).

7.4 Phosphorus, organic, total (mg/L) = phosphorus, total (mg/L) — phosphorus, orthophosphate plus hydrolyzable, total (mg/L).

8. Report

Report phosphorus, hydrolyzable, dissolved (00672); phosphorus, hydrolyzable, total (00669); phosphorus, organic, dissolved (00673); and phosphorus, organic, total (00670), as follows: less than 1 mg/L, two decimals; 1 mg/L and above two significant figures.

9. Precision

See the individual methods: phosphorus, orthophosphate, dissolved or total; phosphorus, orthophosphate plus hydrolyzable, dissolved or total; and phosphorus, dissolved or total. Precision will depend on the precision obtained for each method.