

84-020 ORTHOPHOSPHATE in water**1. Application**

- 1.1 This colorimetric method is applicable to surface and groundwater with orthophosphate levels in the range from 1 $\mu\text{g/L}$ to 500 $\mu\text{g/L}$ P. Samples having higher concentrations than this can be measured by appropriate dilution of an aliquot. The only known interferences with the method are mercury and arsenic: Mercury at levels above 1 mg/L Hg gives a precipitation of mercurous chloride and mercury in the reduction step. This is not a problem with natural waters unless mercury chloride has been used to "preserve" the sample. At the concentration of sulphuric acid used in the method, silica does not interfere.

2. Apparatus

- 2.2 Technicon autoanalyser unit consisting of:
- 2.2.1 Sampler
 - 2.2.2 Manifold
 - 2.2.3 Proportioning pump
 - 2.2.4 Colorimeter with a 50 mm flow cell and 660 μm filter.
 - 2.2.5 Recorder

3. Reagents

- 3.1 Ammonium molybdate solution (NH_4) $\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$: Dissolve 25 g ammonium molybdate in 175 mL distilled water; to 400 mL distilled water add 280 mL concentrated H_2SO_4 . Add the molybdate solution to the acid solution and dilute to 1 liter.
- 3.2 Stannous chloride ($\text{ZnCl}_2\cdot 2\text{H}_2\text{O}$) stock solution: Dissolve 5g of stannous chloride in 25 mL concentrated hydrochloric acid and dilute to 500 mL with distilled water; this stock solution is stable for 2 weeks at 5°C storage.
- 3.3 Stannous chloride working solution: To 30 mL stock solution (3.2) add 25 mL concentrated hydrochloric acid and dilute to 500 mL with distilled water; this solution is stable for 12 hours and generally is sufficient quantity for 1 day.

3.4 Phosphorus standards:

- 3.4.1 Stock phosphorus solution, 1000 $\mu\text{g/mL P}$: Dissolve 4.393 g of anhydrous potassium dihydrogen phosphate, KH_2PO_4 (oven-dried at 105°C), in distilled water and dilute to 1 liter. Store in amber or dark-coloured bottle. Alternatively certified atomic absorption standards can be used.
- 3.4.2 Intermediate phosphorus solution, 10 $\mu\text{g/mL P}$: Pipette 10 mL stock solution (3.4.1) into a 1 liter volumetric flask and dilute to the mark.
- 3.4.3 Standard phosphorus solution, 1000 $\mu\text{g/L P}$: Pipette 50 mL intermediate solution (3.4.2) into a 500 mL volumetric flask and dilute to the mark; prepare daily.
- 3.4.4 Working phosphorus solution: Using the standard solution (3.4.3) prepare the following working solutions in 100 mL volumetric flasks:

mL of standard solution (1000 $\mu\text{g/L P}$)	Concentration ($\mu\text{g/L}$)
0	0
0.5	5
1.0	10
3.0	30
5.0	50

4. Procedure

4.1 Sample preparation

- 4.1.1 The sample should be cooled to about 4°C as soon as it has been taken and analysis should be carried out the same day.
- 4.1.2 The sample aliquot used for the analysis should be either free from turbidity or filtered through a 0.45 μm membrane filter.

4.2 Determination of Orthophosphate by autoanalyser.

- 4.2.1 Run the standards and samples at 20 samples per hour using the manifold shown in Figure 4.
- 4.2.2 Check that the correct filters and aperature are in the colorimeter: 660 $\text{m}\mu$; aperature (reference side) No. 4-7.
- 4.2.3 Turn on colorimeter lamp and allow at least 30 minutes to warm-up before running baseline as in 4.2.11 below.

- 4.2.4 Place proper manifold on pump and attach all connections.
- manifold to sampler
 - colorimeter to manifold return
 - manifold to sampler wash receptable
 - manifold, colorimeter, and wash receptable overflow to waste sink.
- 4.2.5 Place all reagent lines in distilled water.
- 4.2.6 Stretch manifold pump tubes, lower pump rollers and start pump. Run for at least 5 minutes with lines in water.
- 4.2.7 Arrange standards and samples on sampler, starting at position No. 1 on the inner rim. Insert U-shaped pin in appropriate numbered hole on the outer rim to stop sampler at the last sample.
- Note: Every time a new stannous chloride working solution is diluted a set of standard solutions must be run. Standard solutions should be run periodically to check the validity of the calibration curve.
- 4.2.8 Insert reagent lines in full reagent bottles. Check with the diagram for proper connections. Put sample line and probe into the wash solution (0.3% H₂SO₄) reagent bottle and let run for about 5 minutes.
- NOTE: During analysis the orthophosphate is reacted with ammonium molybdate to form heteropolymolybdophosphoric acid H₃(PMo₃O₁₀)₄. This is then reduced with stannous chloride in aqueous sulphuric acid medium to form molybdenum blue.
- 4.2.9 Turn on pen drive of recorder (bottom switch). Top switch must never be turned off.
- 4.2.10 Check zero adjustment with zero aperture on sample side of colorimeter. Adjust pen to 0% transmittance (T) by means of the zero control on the colorimeter. Remove the zero aperture.
- 4.2.11 With reagents running and sample line in wash solution, establish baseline at 100% transmittance by means of 100% T control on the colorimeter.
- 4.2.12 Check the gain on recorder and adjust if necessary.
- 4.2.13 When reagent baseline is satisfactory, switch on the sampler.
- 4.2.14 Shut off sampler after last sample has been taken, stopping the probe in the wash receptacle.

- 4.2.15 When the last sample has been recorded, shut off the pen drive (bottom switch) and, if work has been completed for the day, the colorimeter lamp.
- 4.2.16 Place sample and reagent lines in detergent solution and run for 15 minutes.
- 4.2.17 Remove sample and reagent lines from detergent solution, place in distilled water and rinse for 15 minutes.
- 4.2.18 Stop pump by raising the roller assembly.
- 4.2.19 Release tension of pump tubes on manifold.
- 4.2.20 Cap all reagent bottles and return to shelf. Remove all samples from sampler. Clean up any spillage.

5. Calculations

- 5.1 Prepare a calibration curve derived from the peak heights obtained with the standard solutions.
- 5.2 Determine the concentration of orthophosphorus in the samples by comparing sample peak heights with the calibration curve.

6. Precision and accuracy

- 6.1 Insufficient data available

7. References

- 7.1 Analytical methods manual, 1979. Inland Waters Directorate Water Quality Branch, Ottawa, Canada.

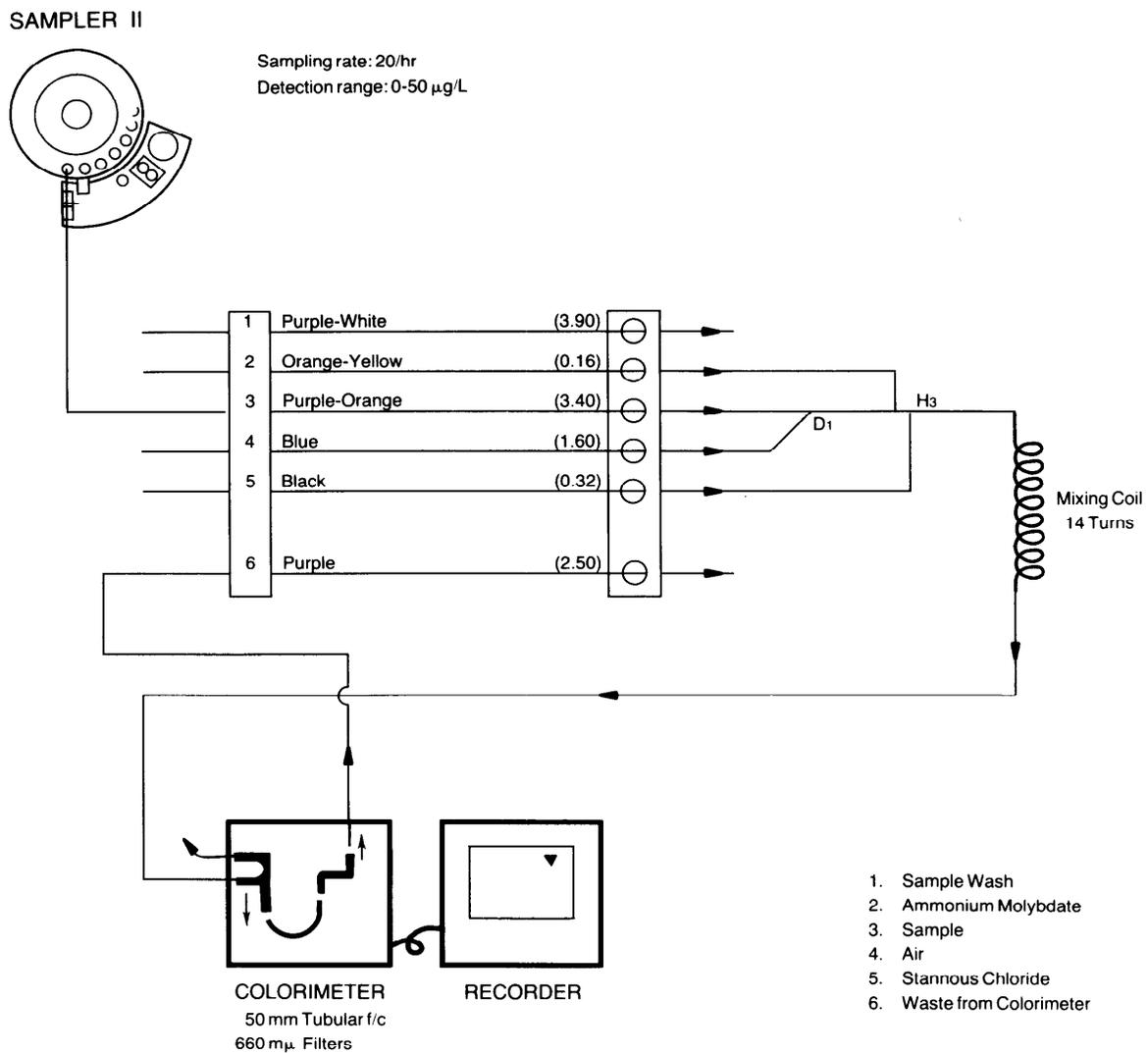


Fig. 4 Flow diagram for the determination of ortho-P in water by an autoanalyser.

Notes