

**METHOD #: 365.4** Pending Approval for NPDES, CWA (Issued 1974)

**TITLE:** Phosphorous, Total (Colorimetric, Automated, Block Digester AA II)

**ANALYTE:** CAS # P Phosphorus 7723-14-0

**INSTRUMENTATION:** Autoanalyzer

**STORET No.** 00665

## 1.0 Scope and Application

1.1 This method covers the determination of total phosphorus in drinking water, surface water and domestic and industrial wastes. The applicable range of this method is 0.01 to 20 mg P/L.

## 2.0 Summary of Method

2.1 The sample is heated in the presence of sulfuric acid,  $K_2SO_4$  and  $HgSO_4$  for two and one half hours. The residue is cooled, diluted to 25 mL and placed on the AutoAnalyzer for phosphorus determination.

## 3.0 Sample Handling and Preservation

3.1 Sample containers may be of plastic material, such as a cubitainer, or of Pyrex glass.

3.2 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 mL of conc.  $H_2SO_4$  per liter and refrigeration at 4°C.

## 4.0 Apparatus

4.1 Block Digester BD-40

4.2 Technicon Method No. 327-74W for Phosphorus

## 5.0 Reagents

5.1 Mercuric sulfate: Dissolve 8 g red mercuric oxide ( $HgO$ ) in 50 mL of 1:4 sulfuric acid (10 conc.  $H_2SO_4$ ; 40 mL distilled water) and dilute to 100 mL with distilled water.

5.2 Digestion solution: (Sulfuric acid-mercuric sulfate-potassium sulfate solution): Dissolve 133 g of  $K_2SO_4$  in 600 mL of distilled water and 200 mL of conc.  $H_2SO_4$ . Add 25 mL of mercuric sulfate solution (5.1) and dilute to 1 liter.

5.3 Sulfuric acid solution (0.72 N): Add 20 mL of conc. sulfuric acid to 800 of distilled water, mix and dilute to 1 liter.

5.4 Molybdate/antimony solution: Dissolve 8 g of ammonium molybdate and 0.2g of antimony potassium tartrate in about 800 mL of distilled water and dilute to

- 1 liter.
- 5.5 Ascorbic acid solution: Dissolve 60 g of ascorbic acid in about 600 mL of distilled water. Add 2 mL of acetone and dilute to 1 liter.
  - 5.6 Diluent water: Dissolve 40 g of NaCl in about 600 mL of distilled water and dilute to 1 liter.
  - 5.7 Sulfuric acid solution, 4%: Add 40 mL of conc. sulfuric acid to 800 mL of ammonia-free distilled water, cool and dilute to 1 liter.

## 6.0 Procedure

### Digestion

- 6.1 To 20 or 25 mL of sample, add 5 mL of digestion solution and mix. (Use a vortex mixer).
- 6.2 Add 4-8 Teflon boiling chips. Too many boiling chips will cause the sample to boil over.
- 6.3 With Block Digester in manual mode set low and high temperature at 160°C and preheat unit to 160°C. Place tubes in digester and switch to automatic mode. Set low temperature timer for 1 hour. Reset high temperature to 380°C and set timer for 2 1/2 hours.
- 6.4 Cool sample and dilute to 25 mL with distilled water. If TKN is determined the sample should be diluted with ammonia-free water.

### Colorimetric Analysis

- 6.4.1 Check the level of all reagent containers to ensure an adequate supply.
- 6.4.2 Excluding the molybdate/antimony line, place all reagent lines in their respective containers, connect the sample probe to the Sampler IV and start the proportioning pump.
- 6.4.3 Flush the Sampler IV wash receptacle with about 25 mL of 4% sulfuric acid (5.7).
- 6.4.4 When reagents have been pumping for at least five minutes, place the molybdate/antimony line in its container and allow the system to equilibrate.
- 6.4.5 After a stable baseline has been obtained, start the sampler.

## 7.0 Calculations

- 7.1 Prepare a standard curve by plotting peak heights of processed standards against concentration values. Compute concentrations by comparing sample peak heights with the standard curve.

## 8.0 Precision and Accuracy

- 8.1 In a single laboratory (EMSL) using sewage sample containing total P at levels of 0.23, 1.33, and 2.0, the precision was  $\pm 0.01$ ,  $\pm 0.04$ , and  $\pm 0.06$ , respectively.
- 8.2 In a single laboratory (EMSL) using sewage samples of concentration 1.84 and 1.89, the recoveries were 95 and 98%, respectively.

## **Bibliography**

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2. Gales, M.E. and Booth, R.L., "Evaluation of Organic Nitrogen Methods", EPA Office of Research and Monitoring, June, 1972.
  3. Gales, M.E. and Booth, R.L., "Simultaneous and Automated Determination of Total Phosphorus and Total Kjeldahl Nitrogen", Methods Development and Quality Assurance Research Laboratory, May, 1974.
  4. Technicon "Total Kjeldahl Nitrogen and Total Phosphorus BD-40 Digestion Procedure for Water", August, 1974.
  5. Gales, M.E., and Booth, R.L., "Evaluation of the Technicon Block Digester System for the Measurement of Total Kjeldahl Nitrogen and Total Phosphorus", EPA-600 /4-78-015, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

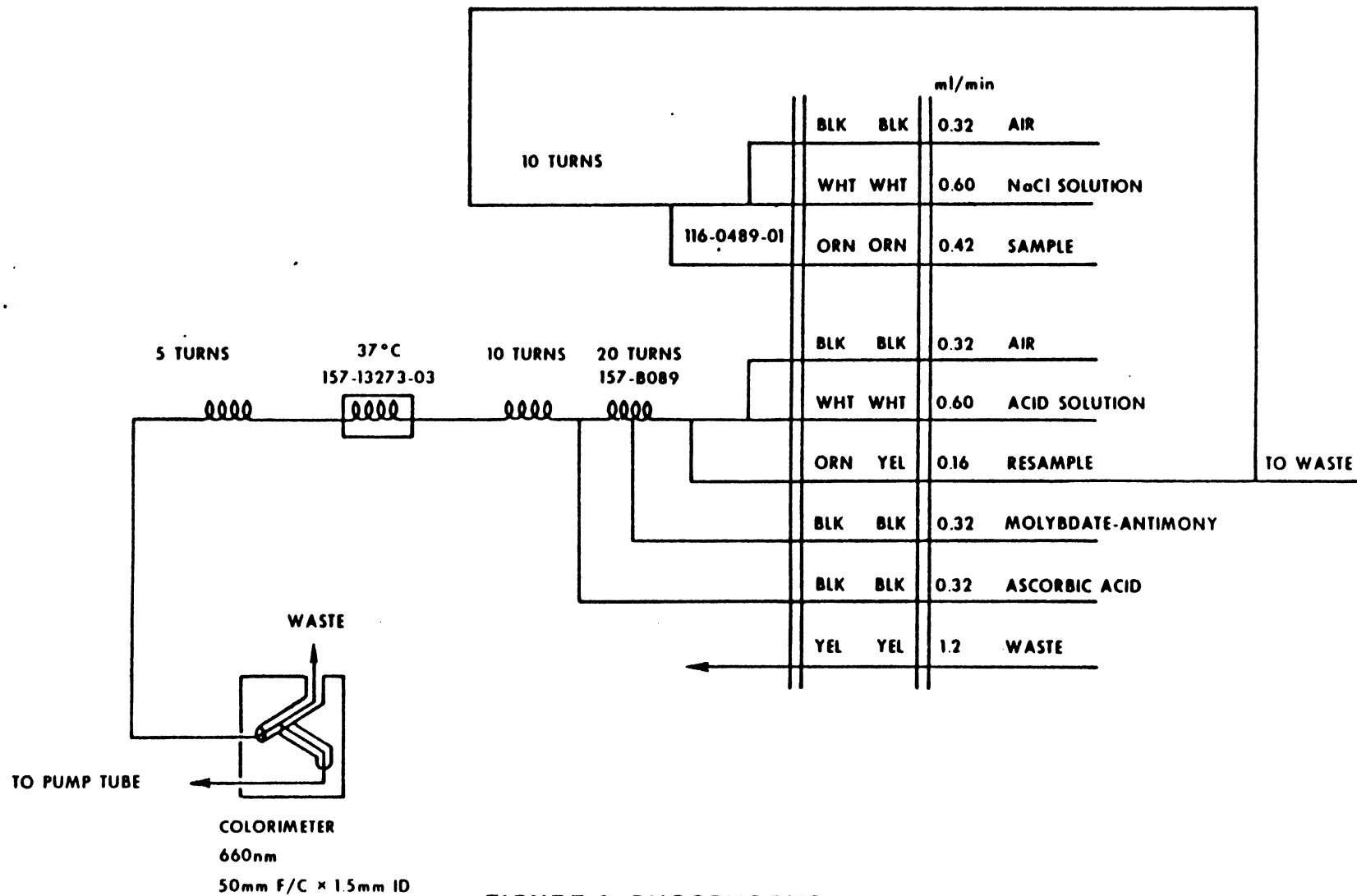


FIGURE 1. PHOSPHORUS MANIFOLD AA11

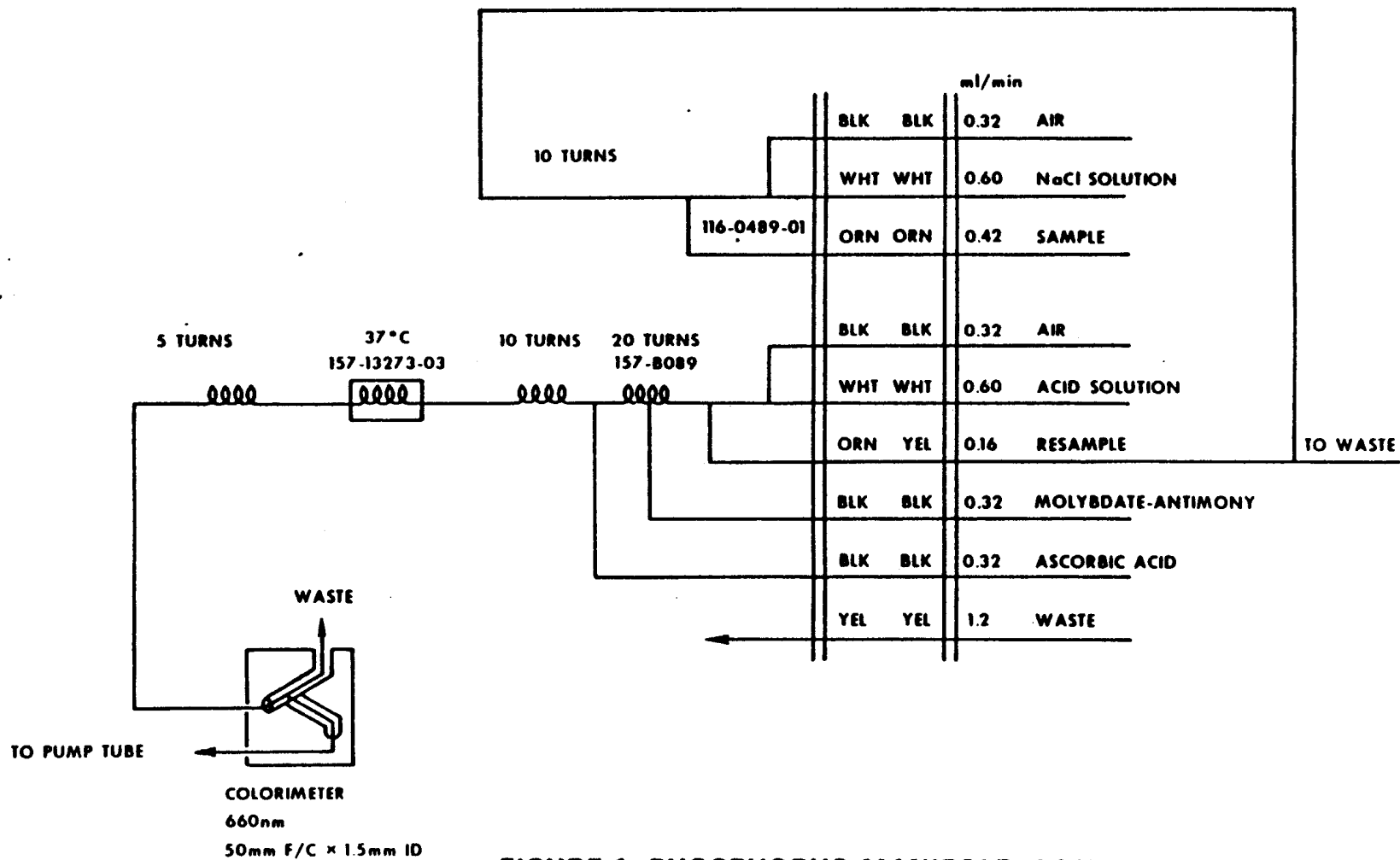


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