



- 4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

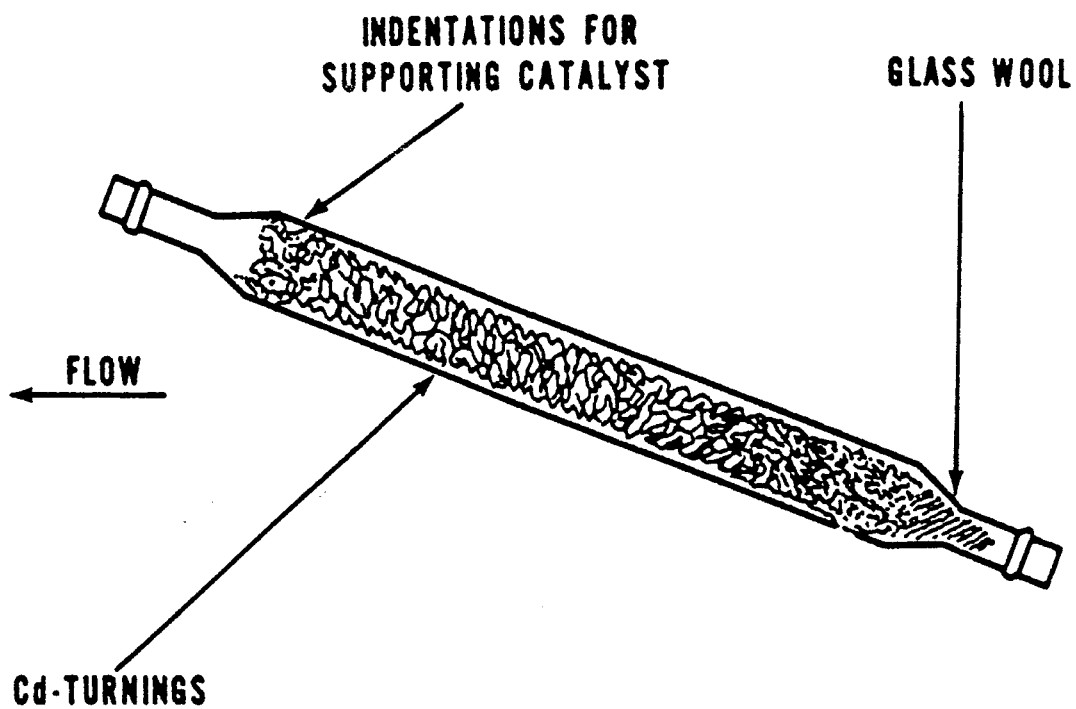
## 5.0 Apparatus

- 5.1 Technicon AutoAnalyzer (AAI or AAI) consisting of the following components:
- 5.1.1 Sampler.
  - 5.1.2 Manifold (AAI) or analytical cartridge (AAI).
  - 5.1.3 Proportioning Pump
  - 5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.
  - 5.1.5 Recorder
  - 5.1.6 Digital printer for AAI (Optional).

## 6.0 Reagents

- 6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).
- 6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (6. 7) and copperized with 2% solution of copper sulfate (6. 8) in the following manner:
- 6.2.1 Wash the cadmium with HCl (6.7) and rinse with distilled water. The color of the cadmium so treated should be silver.
  - 6.2.2 Swirl 10 g cadmium in 100 mL portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.
  - 6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.
- 6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20° incline to minimize channeling. See Figure 1.
- 6.4 Preparation of reduction column AAI: The reduction column is a U-shaped, 35 cm length, 2 mm I.D. glass tube (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper- cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system.
- NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.
- 6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

- 6.6 Color reagent: To approximately 800 mL of distilled water, add, while stirring, 100 mL conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.
- 6.7 Dilute hydrochloric acid, 6N: Dilute 50 mL of conc. HCl to 100 mL with distilled water.
- 6.8 Copper sulfate solution, 2%: Dissolve 20 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500 mL of distilled water and dilute to 1 liter.
- 6.9 Wash solution: Use distilled water for unpreserved samples. For samples preserved with  $\text{H}_2\text{SO}_4$ , use 2 mL  $\text{H}_2\text{SO}_4$  per liter of wash water.
- 6.10 Ammonium chloride-EDTA solution: Dissolve 85 g of reagent grade ammonium chloride and 0.1 g of disodium ethylenediamine tetraacetate in 900 mL of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter. Add 1/2 mL Brij-35 (available from Technicon Corporation).



TILT COLUMN TO 20° POSITION

FIGURE 1. COPPER CADMIUM REDUCTION COLUMN  
(1 1/2 ACTUAL SIZE)

- 6.11 Stock nitrate solution: Dissolve 7.218 g KNO<sub>3</sub> and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 mL of chloroform per liter. Solution is stable for 6 months. 1 mL = 1.0 mg NO<sub>3</sub>-N.
- 6.12 Stock nitrite solution Dissolve 6.072 g KNO<sub>2</sub> in 500 mL of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 mL of chloroform and keep under refrigeration. 1.0 mL = 1.0 mg NO<sub>2</sub>-N.
- 6.13 Standard nitrate solution: Dilute 10.0 mL of stock nitrate solution (6.11) to 1000 mL. 1.0 mL = 0.01 mg NO<sub>3</sub>-N. Preserve with 2 mL of chloroform per liter. Solution is stable for 6 months.
- 6.14 Standard nitrite solution: Dilute 10.0 mL of stock nitrite (6.12) solution to 1000 mL. 1.0 mL = 0.01 mg NO<sub>2</sub>-N. Solution is unstable; prepare as required.
- 6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 mL volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Conc., mgNO <sub>2</sub> -N or NO <sub>3</sub> -N/L	mL Standard Solution/100 mL
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl- 24.53 g/L	MgCl <sub>2</sub> - 5.20 g/L	Na <sub>2</sub> SO <sub>4</sub> - 4.09 g/L
CaCl <sub>2</sub> - 1.16 g/L	KCl - 0.70 g/L	NaHCO <sub>3</sub> - 0.20 g/L
Kbr - 0.10 g/L	H <sub>3</sub> BO <sub>3</sub> - 0.03 g/L	SrCl <sub>2</sub> - 0.03 g/L
NaF- 0.003 g/L		

## 7.0 Procedure

- 7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH<sub>4</sub>OH.
- 7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in 20- incline position (AAI). Care should be taken not to introduce air into reduction column on the AAII.
- 7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

NOTE 3: Condition column by running 1 mg/L standard for 10 minutes if a

new reduction column is being used. Subsequently wash the column with reagents for 20 minutes.

- 7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.
- 7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAIL, use a 40/hr, 4:1 cam and a common wash.
- 7.6 Switch sample line to sampler and start analysis.

## 8.0 Calculations

- 8.1 Prepare appropriate standard curve or curves derived from processing NO<sub>2</sub> and/or NO<sub>3</sub> standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

## 9.0 Precision and Accuracy

- 9.1 Three laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate mg N/liter	Precision as Standard Deviation mg N/liter	Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+ 18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	- 2.69	-0.067

## Bibliography

1. Fiore, J., and O'Brien, J. E., "Automation in Sanitary Chemistry - parts 1 & 2 Determination of Nitrates and Nitrites", *Wastes Engineering* 33, 128 & 238 (1962).
2. Armstrong, F. A., Stearns, C. R., and Strickland, J. D., "The Measurement of Upwelling and Subsequent Biological Processes by Means of the Technicon AutoAnalyzer and Associated Equipment", *Deep Sea Research* 14, p 381-389 (1967).
3. Annual Book of ASTM Standards, Part 31, "Water", Standard D1254, p 366 (1976).
4. Chemical Analyses for Water Quality Manual, Department of the Interior, FWPCA, R. A. Taft Sanitary Engineering Center Training Program, Cincinnati, Ohio 45226 (January, 1966).
5. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1141-75, Substitute Ocean Water, p 48 (1976).

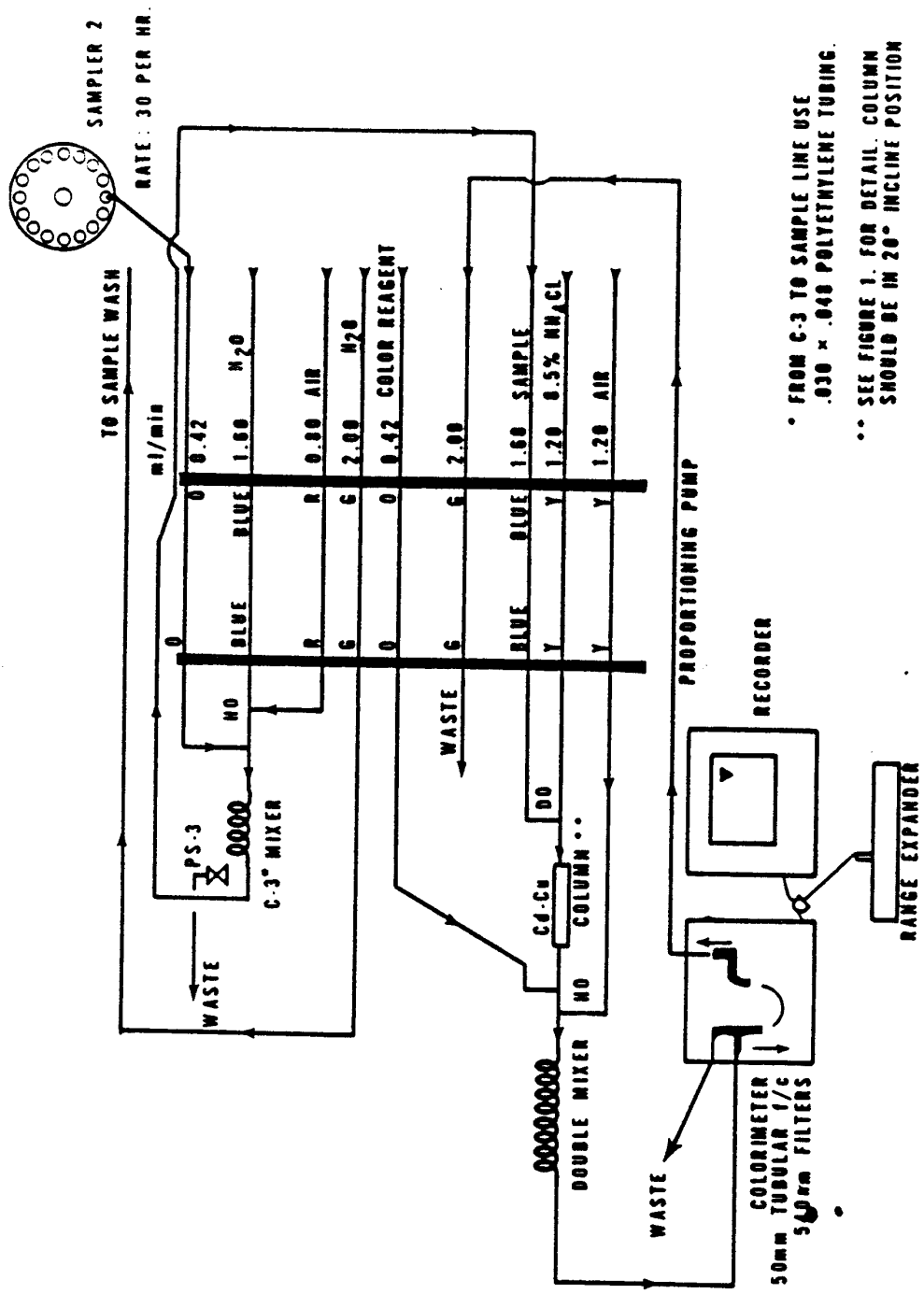


FIGURE 2. NITRATE - NITRITE MANIFOLD AA-1

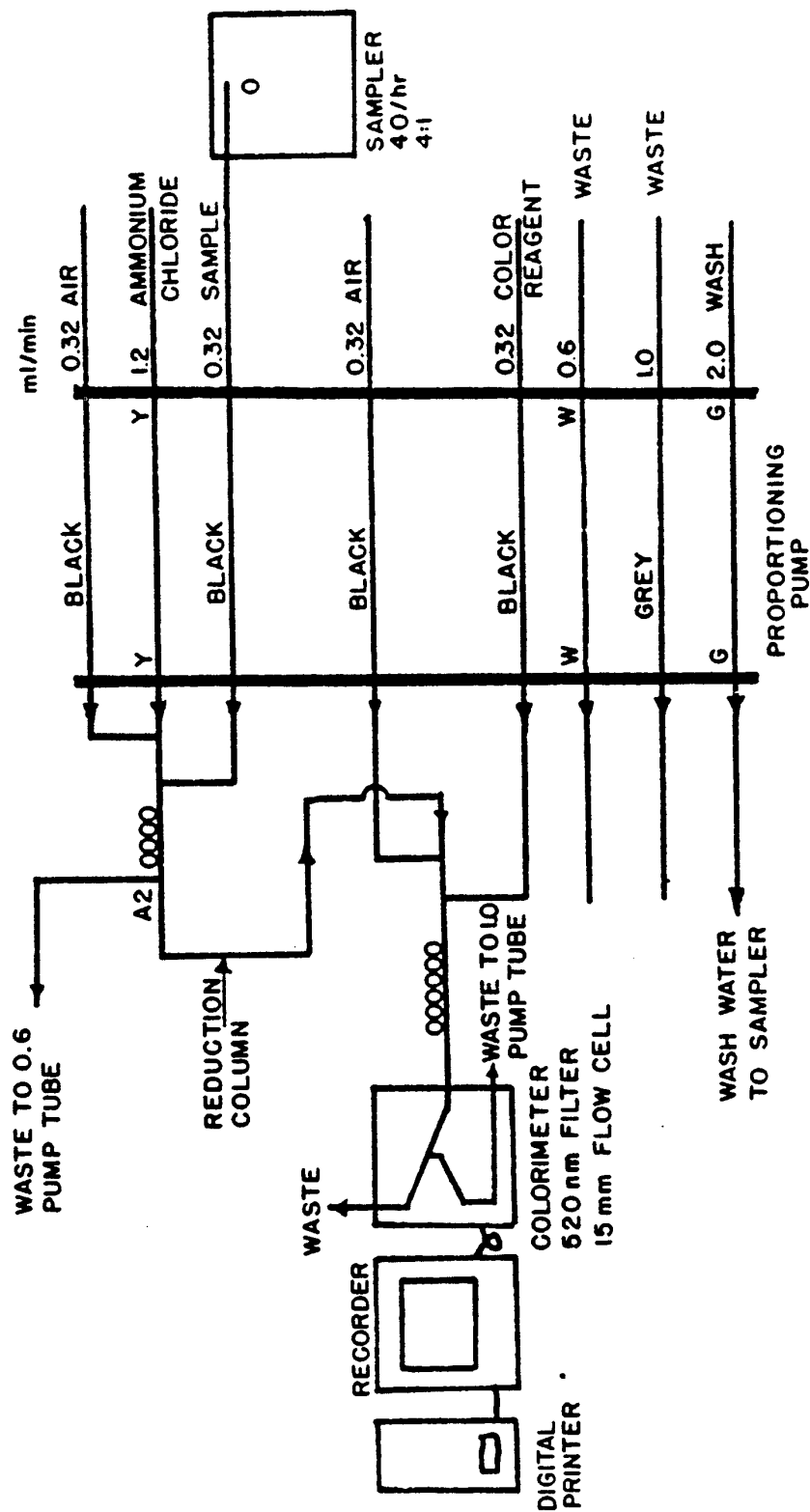


FIGURE 3 NITRATE-NITRITE MANIFOLD AA II