

84-022 AMMONIA and NITRATE in water**1. Application**

- 1.1 This automated method is applicable to the determination of ammonium and nitrate in surface and ground water in the range of 0-5 $\mu\text{g/mL}$ and 0-20 $\mu\text{g/mL}$ respectively. The sample containers should be tightly capped immediately after the sample is collected and analysis carried out the same day. If this is not possible store samples at 4°C.

2. Apparatus

- 2.1 Technicon auto-analyser unit consisting of:
- 2.1.1 Sampler
 - 2.1.2 Manifold and distillation apparatus
 - 2.1.3 Proportioning pump
 - 2.1.4 Colorimeters with flow cells (Ammonia 50 mm and nitrate 15 mm) and 570 m μ filters.
- 2.2 Oil bath (115°C).

3. Reagents

- 3.1 Lithium acetate buffer: Dissolve 335.7 g of lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$) slowly with stirring in 545 mL of glacial acetic acid. Dilute with distilled water until volume is near 2 liters. Allow to cool and check the pH (it should read between 5.0-5.5) adjust if necessary and make to final volume of 2 liters. Filter this solution to remove fine particles.
- 3.2 Ninhydrin: Dissolve 16 g of ninhydrin in 600 mL of dimethyl sulfoxide (DMSO). Add 160 mL lithium acetate buffer. Add 36 mL of glacial acetic acid to a pH of 8.0. Use more acetic acid if necessary. Make up to 1 liter with distilled water. Store in an amber bottle open to air. The reagent is stable for months at room temperature.
- 3.3 Hydrazine Sulfate solution ($\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{SO}_4$): Dilute 0.52 g of hydrazine sulfate in a liter volumetric flask with distilled water. Add 2-3 drops of concentrated sulfuric acid. Store in an acid washed borosilicate glass bottle.
- 3.4 Titanous chloride solution, 20%: Dilute 15 mL of 20% titanous chloride stock solution to 100 mL in volumetric flask with distilled water. This is made up fresh each day.

- 3.5 0.5N Sodium Hydroxide (NaOH): Dilute 20 g of sodium hydroxide in a liter volumetric flask with distilled water.
- 3.6 0.1N Hydrochloric Acid (HCl): Dilute 8.9 mL of concentrated hydrochloric in a liter volumetric flask with distilled water. This acid is used to convert NH_3 gas from the distillation apparatus back to solution.
- 3.7 Levor IV wetting agent.
- 3.8 Standard (ammonium and nitrate - N) solution: Dissolve 2.3596 g of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ and 3.611 g of potassium nitrate KNO_3 in water, dilute the solution to a volume of 500 mL in a volumetric flask, and mix the solution thoroughly. If pure, dry reagents are used, this solution contains 1000 $\mu\text{g}/\text{mL}$ of ammonium - N and 1000 $\mu\text{g}/\text{mL}$ of nitrate - N. Store this solution in a refrigerator.

4. Procedure

- 4.1 **Determination of NH_4 and NO_3 by autoanalyser.**
- 4.1.1 Check that the correct filters and aperature are in the colorimeter: 570 μm and No. 7 aperature (reference side).
- 4.1.2 Turn on colorimeter lamp and allow at least 30 minutes to warm up before running baseline as in 4.1.10 below.
- 4.1.3 Allow the oil bath to reach 115°C before starting the proportioning pump. This is done because the glass to teflon parts have to be hot to seal the distillation apparatus joints.
- 4.1.4 Place proper manifold on pump and attach all connections.
- a) manifold to sampler
 - b) manifold to sampler wash receptacle
 - c) manifold, colorimeter, and wash receptacle overflow to waste sink
 - d) connect manifold to heating bath (115°C) and distillation system
 - e) connect manifold to delay coil in heating bath 95°C
 - f) connect heating bath to jacketed mixer to colorimeter
 - g) connect cooling bath (72°C) to jacketed mixer.
- 4.1.5 Place all reagent lines in distilled water.
- 4.1.6 Stretch manifold pump tubes, lower pump rollers and start pump. Run for at least 5 minutes with lines in water.
- 4.1.7 Arrange standards and samples on sampler, starting at position No. 1 on the inner rim. Insert U-shaped pin in appropriately numbered hole on the outer rim to stop sampler at the last sample.

- 4.1.8 Insert reagent lines in full reagent bottles. Check with Fig. 9 for correct connections. Distilled water is used as sample wash.
- 4.1.9 Turn on pen drive of recorder (bottom switch). Top switch must never be turned off.
- 4.1.10 Check zero adjustments 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.
- 4.1.11 With reagents running and sample line in distilled water establish a baseline at 100% transmittance (T) by means of the 100% T control on the colorimeter.
- 4.1.12 Check the gain on the recorder and adjust it if necessary.
- 4.1.13 When reagent baseline is satisfactory, switch on sampler.
- 4.1.14 Shut off the sampler after the last sample has been taken, stopping the probe in the wash receptacle (or transfer the probe to a container of distilled water).
- 4.1.15 When the last sample has been recorded, shut off the pen drive (bottom switch) and, if work has been completed the colorimeter lamp.
- 4.1.16 Place sample and reagent lines in detergent solution and run for 15 minutes. Rinse sample and reagent lines with 10% HCl for 15 minutes. Remove sample and reagent lines from acid rinse, place in distilled water and rinse for 15 minutes.
- 4.1.17 Stop pump and raise roller assembly.
- 4.1.18 Release tension of pump tubes on manifold.
- 4.1.19 Cap all reagent bottles and return to shelf. Remove all samples from sampler and clean up any spillage.
- 4.1.20 Prepare standard curve from recorded readings of standards and calculate $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in samples.

5. Calculations

- 5.1 $\mu\text{g/mL NH}_4 \text{ \& } \text{NO}_3 = \text{ } \mu\text{g/mL in sol'n} \times \text{dil.}$
- 5.2 $\mu\text{g/mL NH}_4 = \text{ } \mu\text{g/mL in sol'n} \times \text{dil.}$
where dil. is the dilution factor.
- 5.3 $\text{NH}_4 \text{ \& } \text{NO}_3 - \text{NH}_4 = \mu\text{g/mL NO}_3$

6. Precision

6.1 Insufficient data available

7. References

- 7.1 J.R. Quinn, J.G.A. Boisvert, and I. Wood 1973. Semi-automated Ninhydrin assay of Kjeldahl Nitrogen. *Analytical Biochemistry* 58, 609-614.
- 7.2 Bremner, J.M. 1965. Inorganic forms of nitrogen In *Methods of Soil Analysis*. C.A. Black, ed. Agron. No. 9, Part 2 pp. 1179-1237.

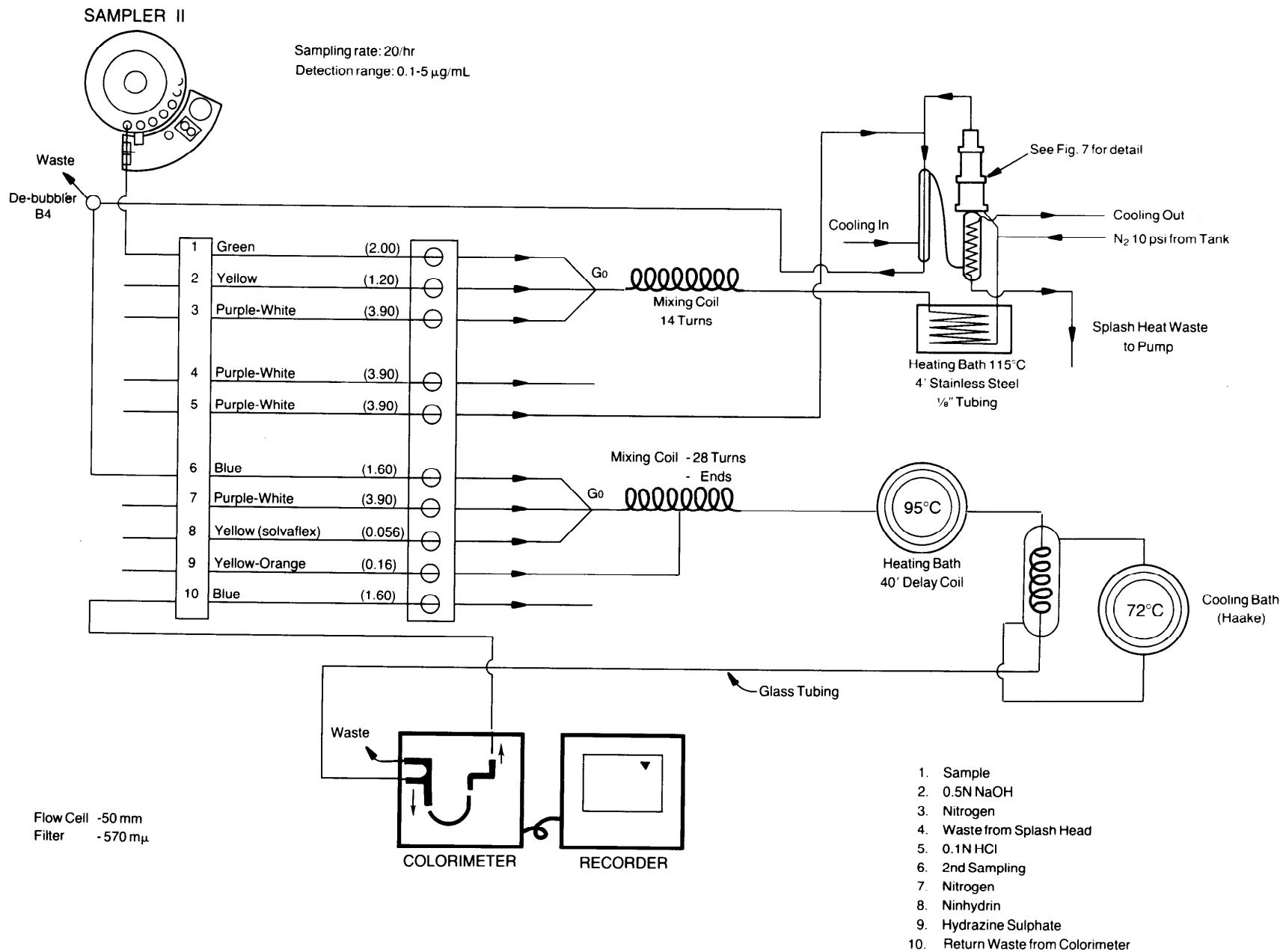


Fig. 8 Flow diagram for the determination of ammonium in water by an autoanalyser.

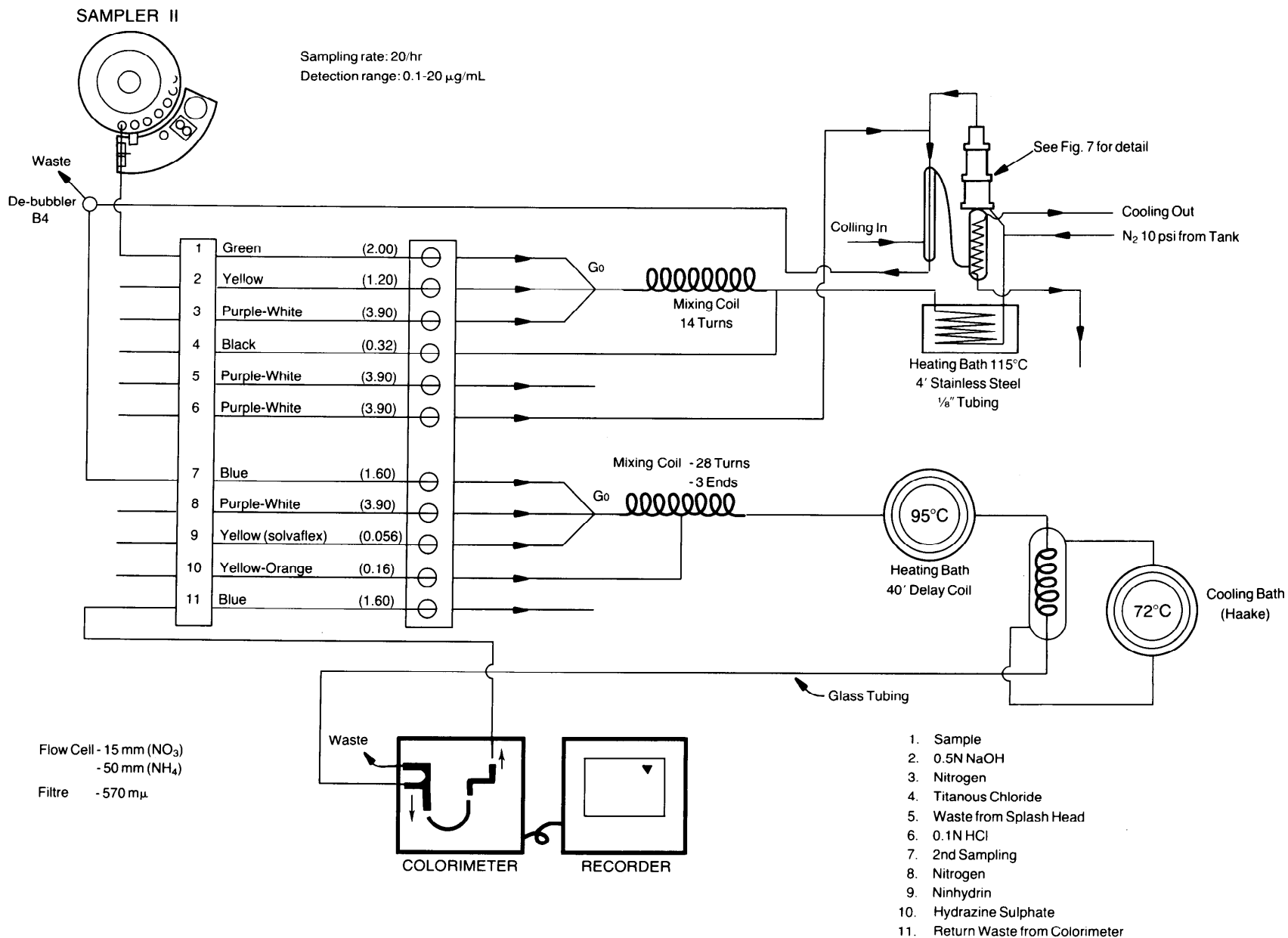


Fig. 9 Flow diagram for the determination of ammonium plus nitrate in water by an autoanalyser.