Methods for Chemical Analysis of Waters and Wastewaters

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PREFACE

This manual describes the analytical procedures for analysing waters and wastewaters now in use in the Water Quality Division laboratories in Ottawa and Burlington, Ontario; Calgary, Alberta; and Moncton, N.B. It was prepared as a joint project of the two Sections of the Water Chemistry Subdivision: the Methods and Properties Section, under P.D. Goulden, which is charged with the responsibility for research and development work on analytical methodology; and the Analytical Services Section, headed by W.J. Traversy, which ensures that methods developed can be used on a regular basis in analytical services laboratories handling large volumes of samples. W.J. Traversy collated the write-ups on methods to form this manual.

The methods are taken from many sources, some with modifications and others developed in the Subdivision, for example, "Determination of Trace Quantities of Nitrilotriacetic Acid by Differential Cathode Ray Polarography" by B.K. Afghan and P.D. Goulden. Other techniques were developed over the years by Mr. W.J. Traversy and others who were connected with the laboratories. To ensure that the manual is used as a working document in the Division's laboratories and to eliminate the necessity of referring to several manuals, each method is written in the format chosen for the project and references are given.

It is intended that this manual will be periodically updated so that the Water Quality Division laboratories and other laboratories that may use it are continually supplied with new methods approved by the Water Chemistry Subdivision.

Methods for determining pesticides, insecticides and certain other organic constituents in waters and wastewaters are not included; chromatographic methods for these will be included in another volume now in preparation.

Comments to improve on the contents and usefulness of this manual are most welcome.

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J.P. Lively
Head
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1 - D = Dissolved (See Metals for explanation)
2 - T = Total (See Metals for explanation)
3 - S = Suspended (See Metals for explanation)
4 - Ex = Extractable (See Metals for explanation)

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ILLUSTRATIONS

ACIDITY

(Titrimetric Method)

1. Scope and Application

1.1. This electrometric titration method is applicable to surface and ground waters. The applicable range is 0.5 to 500 mg/l acidity as $CaCO_3$. The upper range can be extended by dilution of the original sample.

2. Principle of Method

2.1. Acid present in a water is measured by titrating a sample aliquot with standard alkali to the designated endpoints of pH 4.5 and 8.3.

3. Interference

3.1. The method is subject to interferences found in acid samples from mine drainage.

4. Sampling Procedure and Storage

4.1. Samples should be collected in polyethylene or pyrex bottles and stored at a low temperature. Determinations should be performed as soon as possible after sampling.

5. Sample Preparation

5.1. The sample aliquot used for the analysis either should be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. pH meter, Radiometer model 28, or equivalent.

6.2. Burette, 25 ml.

6.3. Magnetic stirrer and stirring bars.

7. Reagents

7.1. Potassium acid phthalate, 0.01N: Dissolve 2.0423 g potassium acid phthalate, $KHC_8H_4O_4$, of the dried salt in distilled water and dilute to 1 litre.

7.2. Sodium hydroxide, saturated, 15N: Dissolve 652 g sodium hydroxide, NaOH, in 800 ml of distilled water and let stand at least 48 hr protected from atmospheric carbon dioxide. Filter through a gooch crucible using a fibre glass filter disc.

7.3. Sodium hydroxide, 1N: Dilute 67 ml 15N NaOH (7.2) to 1 litre with distilled water. Protect from atmospheric carbon dioxide with a soda lime tube.

7.4. Sodium hydroxide, 0.02N: Dilute 20 ml 1N NaOH (7.3) to 1 litre with distilled water and standardize as follows:

7.4.1. Pipette three 20-ml aliquots of the 0.01N potassium acid phthalate (7.1) into 150-ml beakers and dilute with approximately 25 ml distilled water. Add a stirring bar and immerse electrodes. Titrate with 0.02N NaOH (7.4) while stirring gently. Continue titrating until a pH of 8.3 is reached and record volume of NaOH used.

$$\text{Normality of NaOH} = \frac{0.01 \times 20}{\text{Vol. of NaOH (average)}}$$

8. Procedure

8.1. Pipette a sample aliquot into a 150-ml beaker (sample size should be such that no more than 25 ml of titrant is needed for the titration). If necessary, add distilled water, to increase volume for immersion of electrodes.

8.2. Immerse electrodes in the sample and titrate to pH 4.5 and then continue the titration to pH 8.3. Record the volumes of 0.02N NaOH required for both end points.

9. Calculations

9.1. Acidity is calculated according to the following:

9.1.1. Acidity, pH 4.5, as mg/l $CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml of sample}}$

Where A = ml of standard NaOH to titrate to pH 4.5
N = normality of NaOH

9.1.2. Acidity, pH 8.3, as mg/l $CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml of sample}}$

Where A = ml of standard NaOH to titrate to pH 8.3
N = normality of NaOH

10. Precision and Accuracy

10.1. FWPCA (11.2) report a standard deviation of ±1.73 mg/l at a level of 21 mg/l acidity ($CaCO_3$) for the titration to pH 8.3.

11. References

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.2. Federal Water Pollution Control Administration, 1969. FWPCA Methods for Chemical Analysis of Water and Wastes, U.S. Department of the Interior, Cincinnati, Ohio.

ALKALINITY

(Potentiometric Titration)

1. Scope and Application

1.1. This potentiometric titration method is applicable to the determination of alkalinity in surface, ground and sea waters in the range 0.5 to 500 mg/l alkalinity as $CaCO_3$. The upper range can be extended by dilution of the original sample.

2. Principle of Method

2.1. Phenolphthalein alkalinity is determined by titration of a sample aliquot with a standard solution of strong acid to a pH of 8.3.

2.2. Total alkalinity (methyl orange) is determined in a water by potentiometric titration of a sample aliquot with a standard solution of strong acid. A two endpoint technique is employed that determines the actual inflection point or equivalence point pH of the titration.

3. Interferences

3.1. There are no known significant interferences.

4. Sampling Procedure and Storage

4.1. The sample container should be tightly capped as soon as the sample has been collected and the alkalinity determined as soon as possible after opening the container in the laboratory, usually the same day.

5. Sample Preparation

5.1. The sample aliquot used for the analyses either should be free from turbidity or should be allowed to settle prior to analyses.

6. Apparatus

6.1. Radiometer automatic titration system (or equivalent) consisting of:

6.1.1. Titrator, model TTT11.

6.1.2. pH meter model 28.

6.1.3. Titration assembly, type TTA1.

6.1.4. Magnetic valve.

6.2. Beakers, 200 ml, tall form.

7. Reagents

7.1. Sulphuric acid solution, 0.2N: Dilute 11.1 ml conc sulphuric acid, H_2SO_4, to 2 litres with distilled water.

7.2. Sulphuric acid standard titrant, 0.01N: Dilute 100 ml 0.2N H_2SO_4 (7.1) to 2 litres with distilled water and standardize.

7.2.1. Standardization of sulphuric acid standard titrant: Dry anhydrous sodium carbonate, Na_2CO_3, overnight at 105°C. Cool in a dessicator, then weigh 1.060 g and dissolve in distilled water and dilute to 1 litre. Pipette 10.0-ml aliquots and titrate with 0.01N H_2SO_4 to pH 4.5 and 4.2, recording volume of acid at pH 4.5 and again at pH 4.2. Calculation of factors: 1.060 g Na_2CO_3 dissolved in 1 litre of distilled water is 1060 mg/1 Na_2CO_3 or 1000 mg/1 $CaCO_3$ i.e., 1 ml = 1.000 mg $CaCO_3$.

Example: pH 4.2, Vol. of acid = 19.47 ml
pH 4.5, Vol. of acid = 19.22 ml
Start, Vol. of acid = 0.00 ml

Calculations: volume of acid needed for titration = $X_1 - (X_2-X_1)$ where X_1 = number of ml of acid needed to titrate to pH 4.5 and X_2 = number of ml of acid needed to titrate to pH 4.2 i.e., total volume of acid used. Thus number of ml of acid used = 19.22 - (19.47-19.22) = 18.97. 18.97 ml of 0.01N H_2SO_4 is therefore equivalent to 10 mg $CaCO_3$ and 1 ml of 0.01N H_2SO_4 is equivalent to 0.514 mg $CaCO_3$.

Factors (F) are:

for 100 ml sample aliquot: $\frac{1000}{100} \times .514 = 5.14$

for 50 ml sample aliquot: $\frac{1000}{50} \times .514 = 10.28$

etc.

8. Procedure

8.1. Using Radiometer titrator;

8.1.1. Pipette a suitable sample aliquot into a 200-ml tall form beaker containing a stirring bar; immerse electrodes into the sample and record pH.

8.1.2. If the pH of the sample is over 8.3, titrate to pH 8.3 and record the volume of acid.

8.1.3. Set Radiometer End Point to pH 4.5
Set Radiometer Proportional Band to 5
Set Radiometer Delay of Shut-Off to 10 sec.
Set Radiometer Range to 20°C.
Turn selector switch to "Read" and Stirrer to "On". Record pH.

Turn selector switch to "Titrate Down Scale" and when "Shut-Off" lamp lights, record volume of acid.
Reset "End-point" to pH 4.2, press "Titrate" button and hold until stirrer reaches normal speed; then release; again when "Shut-Off" lamp lights, record volume of acid.

9. Calculations

9.1. Calculate the alkalinity in the sample as follows:

9.1.1. Phenolphthalein alkalinity = FxV

where alkalinity is expressed as mg/l $CaCO_3$,

F is factor obtained from standardization of acid (7.2.1.)
V = ml of acid needed to titrate to pH 8.3.

9.1.2. Total alkalinity = $F [X_1 - (X_2 - X_1)]$

where alkalinity is expressed as mg/l $CaCO_3$, and

F is factor obtained from standardization of acid (7.2.1.)
X_1 = ml of acid needed to titrate to pH 4.5
X_2 = ml of acid needed to titrate to pH 4.2 i.e., total volume of acid

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division) the coefficient of variation at a concentration of 33.3 mg/l $CaCO_3$ was ±1.48%.

11. Reference

11.1. Thomas J.F.J. and Lynch J.J. 1960. Determination of Carbonate Alkalinity in Natural Waters. Journal of A.W.W.A. 52:259-268.

ALUMINUM

(Colourimetric Ferron Method)

1. Scope and Application

1.1. This method can be applied to the determination of aluminum in surface and ground waters. The applicable range is 0.01 to 1.5 mg/l Al. The upper range can be extended by dilution of the original sample.

2. Principle of Method

2.1. Ferron, 8-hydroxy -7-iodo-5 quinoline sulphonic acid, reacts with aluminum to give a complex that absorbs light in the ultraviolet range. The method is subject to significant interference from iron, but this effect can be greatly minimized by adding orthophenanthroline. This reagent also has the additional advantage that iron may be simultaneously determined.

3. Interferences

3.1. Iron interferes in this method but its effect can be calculated and a correction made. Several other metals and anions show small interference effects, but only manganese and fluoride show sufficiently pronounced effects to require correction. The addition of a beryllium salt minimizes the interference of fluoride.

3.2. Manganese and fluoride should be determined before aluminum so that the necessary corrections may be applied (See calculations 9).

4. Sampling Procedure and Storage

4.1. See Metals, section 4.

5. Sample Preparation

5.1. See Metals, section 5.

6. Apparatus

6.1. Spectrophotometer suitable for use at wavelengths of 370 mu and 520 mu.

7. Reagents

7.1. Hydroxylamine-hydrochloric acid solution: Dissolve 100 g hydroxylamine-hydrochloride, $NH_2OH.HCL$, in distilled water. Add 40 ml conc HCl and 1 g Beryllium sulphate, $BeSO_4.2H_2O$, (1.3 g $BeSO_4.4H_2O$), and dilute to 1 litre.

7.2. Ferron-orthophenanthroline solution: Add 0.5 g ferron and 1.0 g orthophenanthroline to 1 litre of distilled water. Shake for several hours until maximum solution is obtained. Allow any solids to settle out and decant clear supernatant for use.

7.3. Sodium acetate solution, 35%: Dissolve 350 g anhydrous sodium acetate, CH_3COONa, (580 g $CH_3COONa.3H_2O$), in distilled water and dilute to 1 litre.

7.4. Stock aluminum solution, 500 mg/l Al: Dissolve 8.792 g potassium aluminum sulphate (also called potassium alum), $K_2Al_2(SO_4)_4.24H_2O$ in distilled water and dilute to 1 litre in a volumetric flask.

7.5. Standard aluminum solution, 10 mg/l Al: Dilute 20.0 ml of stock solution (7.4) to 1 litre in a volumetric flask using distilled water. Prepare daily.

8. Procedure

8.1. Pipette two 25-ml sample aliquots into separate beakers (one is the test sample; the other is the colour correction sample).

8.2. Prepare a reagent blank using 25 ml distilled water and prepare standards (25 ml) to cover the range 0.05-1.5 mg/l aluminum. Also prepare iron standards (25 ml) to cover the range 0.05-1.5 mg/l for iron correction.

8.3. Add 2.0 ml hydroxylamine-hydrochloride reagent (7.1) to all beakers. Let stand for 30 minutes.

8.4. Add 5.0 ml ferron-orthophenanthroline solution (7.2) to reagent blank, test sample and all standards. Add 5 ml distilled water to colour correction sample.

8.5. Add 2.0 ml sodium acetate solution (7.3) to all beakers. Stir and let stand for at least 10 minutes, but not more than 30 minutes before reading.

8.6. Read test sample, and aluminum standards against reagent blank at 370 mu.

8.7. Read test sample, and iron standards against reagent blank at 520 mu.

8.8. Read colour correction sample at 370 mu (for aluminum) and at 520 mu (for iron) against distilled water. Subtract reading at 370 mu from previous reading obtained on test sample for aluminum (8.6); subtract reading at 520 mu from previous reading obtained on test sample for iron (8.7).

9. Calculations

9.1. Prepare calibration curves for aluminum and iron derived from the absorbancies obtained with the standard solutions.

9.2. Determine the concentrations of apparent aluminum and iron in the sample by comparing sample peak height (subtract colour correction reading) with the calibration curve.

9.3. Mg/l Aluminum

= apparent mg/l Al - (0.12 x mg/l Fe) - (0.04 x mg/l Mn) + (0.05 x mg/l F).

10. Precision and Accuracy

Not available at this time.

11. Reference

11.1. United States Department of the Interior, 1960. Methods for Collection and Analysis of Water Samples. Geological Survey Water - Supply Paper 1454.

ARSENIC

(Silver Diethyldithiocarbamate Method)

1. Scope and Application

1.1. This method is applicable to surface and ground waters. The applicable range is 5 to 80 ug/l As. The upper range can be extended by dilution of the original sample.

2. Principle of Method

2.1. Inorganic arsenic is reduced to arsine, AsH_3, by zinc in acid solution in a generator. The arsine is then passed through a scrubber containing glass wool impregnated with lead acetate solution and into an absorber tube containing silver diethyldithiocarbamate dissolved in pyridine. In the absorber, arsenic reacts with the silver salt forming a soluble red complex that is suitable for photometric measurement.

3. Interferences

3.1. There are no known significant interferences in normal waters. Heavy metals, particularly antimony, could interfere if present in large quantities.

3.2. There is no interference from antimony in concentrations of up to 20 ug/l on arsenic concentrations of 10 and 50 ug/l.

4. Sampling Procedure and Storage

4.1. No special precautions.

5. Sample Preparation

5.1. The sample aliquot used for the analysis should be free from turbidity or filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Arsine generator and absorption tube. See Figure 1.

6.2. Spectrophotometer for use at 540 mu with 1-cm cells.

7. Reagents

7.1. Hydrochloric acid, HCl, concentrated.

7.2. Potassium iodide: Dissolve 15 g potassium iodide, KI, in 100 ml distilled water. Prepare fresh daily.

7.3. Stannous chloride: Dissolve 40 g arsenic - free stannous chloride, $SnCl_2.2H_2O$, in 25 ml conc HCl. Dilute to 100 ml with distilled water.

7.4. Lead acetate solution: Dissolve 10 g lead acetate, $Pb(C_2H_3O_2)_23H_2O$, in 100 ml distilled water.

7.5. Silver diethyldithiocarbamate (SDDC): Dissolve 1 g silver diethyldithiocarbamate, $AgSCSN(C_2H_5)$, in 200 ml pyridine. Store in amber bottle.

7.6. Zinc, Zn, 20-30 mesh, arsenic free.

7.7. Stock arsenic, 1000 mg/l As: Dissolve 1.320 g arsenic trioxide, As_2O_3, in 10 ml distilled water containing 4 g NaOH, and dilute to 1 litre with distilled water.

7.8. Intermediate arsenic solution, 10 mg/l As: Dilute 10 ml arsenic stock (7.7) to 1 litre with distilled water.

7.9. Working arsenic solution, 1 mg/l As: Dilute 10 ml arsenic intermediate solution (7.8) to 100 ml with distilled water.

8. Procedure

8.1. Prepare a series of standards to cover the range 5 to 80 ug/l and also a reagent blank (100 ml distilled water). The standards may be pipetted directly into the flasks and the volume made up with distilled water.

8.2. Pipette a 100-ml sample into a clean generator flask.

8.3. Add 15 ml conc HCl to standards and sample, swirling contents after addition.

8.4. Add 2.0 ml KI solution, swirl contents.

8.5. Add 1.0 ml $SnCl_2$ reagent, swirl contents, and allow 1 hour for reduction.

8.6. Impregnate the glass wool in scrubbers with lead acetate solution. Do not saturate as flow-over from generation will cause turbidity in SDDC reagent.

8.7. Pipette 4.0 ml SDDC reagent into absorber tubes.

8.8. Arrange apparatus as shown in Figure 1.

8.9. Add 15 g zinc metal to generators and connect the scrubber-absorber assemblies immediately. Make certain that all connections are tightly fitted.

8.10. Allow 30 minutes for complete evolution of arsine.

8.11. Measure the absorbance of the solutions at 540 mu using the reagent blank as a reference.

9. Calculations

9.1. Prepare a calibration curve derived from the readings obtained with the standard solutions.

9.2. Determine the concentration of arsenic in the sample by comparing sample reading with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division) the coefficients of variation at arsenic levels of 20 and 70 ug/l were ±6.51% and ±3.63% respectively.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

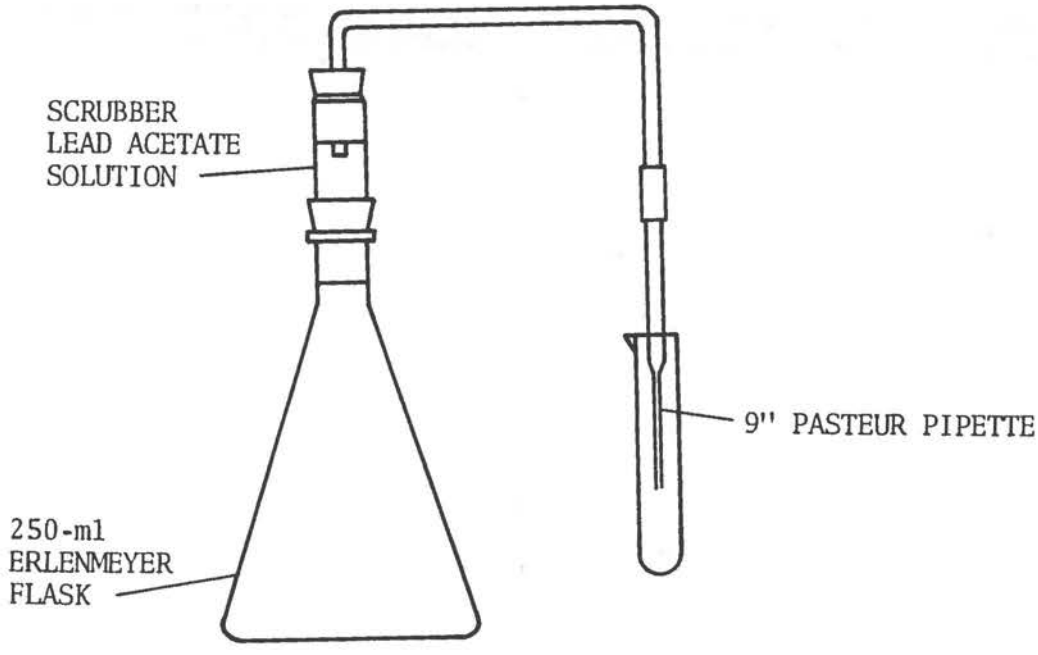

Figure 1 Arsenic generator and absorber assembly

BORON

(Colourimetric Curcumin Method)

1. Scope and Application

1.1. This method is applicable to surface and ground waters in the range 0.0 to 1.0 mg/l. Higher concentrations may be determined using an appropriate dilution of the original sample.

2. Principle of Method

2.1. The red coloured product called rosocyanine, obtained when a sample of water containing boron is acidified and evaporated in the presence of curcumin, is taken up in ethyl alcohol and measured in a spectrophotometer.

3. Interferences

3.1. Nitrate concentrations above 20 mg/l NO_3 interfere with this method. There are no other serious interferences.

4. Sampling Procedure and Storage

4.1. Samples should be stored in polyethylene bottles.

5. Sample Preparation

5.1. The sample aliquot used for analysis either should be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Spectrophotometer for use at 540 mu and a minimum light path of 1 cm.

6.2. Evaporating dishes, 45-150-ml capacity, of vycor glass or platinum.

6.3. Water bath, set at 55° ±2°C.

6.4. Glass stoppered volumetric flasks, 25-ml capacity.

7. Reagents

7.1. Stock boron solution, 100 mg/l B: Dissolve 0.5716 g anhydrous boric acid, H_3BO_3, in distilled water and dilute to 1 litre. Because anhydrous H_3BO_3 loses weight on drying at 150°C, use a reagent meeting ACS specifications and keep the bottle tightly stoppered to prevent the entrance of air moisture.

7.2. Standard boron solution, 1.0 mg/l B (1.0 ml = 1.0 ug B): Dilute 10.00 ml stock boron solution to 1 litre with distilled water.

7.3. Curcumin reagent: Dissolve 0.040 g finely ground curcumin and 5.0 g oxalic acid, $C_2H_2O_4.2H_2O$, in 80 ml of 95 per cent ethyl alcohol. Add 4.2 ml conc HCl and make the solution up to 100 ml with ethyl alcohol in a 100-ml volumetric flask. (Isopropyl alcohol, 95 per cent, may be used in place of ethyl alcohol.) This reagent will be stable for several days, if stored in a refrigerator.

7.4. Ethyl alcohol, C_2H_5OH, 95 per cent.

8. Procedure

8.1. To prepare calibration curve, pipette 0.00 (blank), 0.25, 0.50, 0.75, and 1.00 ug standard boron solution (7.2) into evaporating dishes (dishes should be of the same size and shape).

8.2. Pipette 1.00 ml sample or dilution into an evaporating dish.

8.3. Add 4.0 ml curcumin reagent to each and swirl dishes gently to mix.

8.4. Float the dishes on a water bath set at 55° ±2°C and evaporate the contents to complete dryness.

8.5. Remove each dish from the water bath as soon as the contents appear dry and the odor of HCl is gone.

8.6. After the dishes cool to room temperature add 10.0 ml 95% ethyl alcohol to each dish, stirring gently with a polyethylene rod to ensure complete dissolution of the red-coloured product.

8.7. Wash the contents of each dish into separate 25-ml volumetric flasks using 95% ethyl alcohol. Make up to the mark on each flask with 95% ethyl alcohol and mix by inverting the flasks.

8.8. Read absorbancies at 540 mu after setting the reagent blank at zero absorbance. Make readings within one hour of drying the samples.

9. Calculations

9.1. Prepare a calibration curve derived from the readings obtained with the standard solutions.

9.2. Determine the concentration of boron in the sample by comparing sample reading with the calibration curve.

10. Precision and Accuracy

10.1. Standard Methods report a standard deviation of ±0.06 mg/l at a boron level of 0.18 mg/l B as determined with nine laboratories.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

CALCIUM

(EDTA Titration)

1. Scope and Application

1.1. This method is applicable to the determination of calcium in surface, ground and sea waters. All calcium concentrations greater than 0.5 mg/l Ca can be measured by using an appropriate sample aliquot.

2. Principle of Method

2.1. When ethylenediamine tetraacetic acid or its sodium salts (EDTA) is added to water containing both calcium and magnesium, it is possible to determine the concentration of both cations or of each. Calcium can be determined directly using EDTA when the pH is made sufficiently high (12-13) so that the magnesium is largely precipitated as the hydroxide and an indicator used which combines with calcium only. Several indicators are available that will give a colour change and in this test CalVer 11 is used as the indicator. When used in the manner described below the indicator forms a pink complex with calcium only, and this complex is changed to the purple of the uncomplexed dye when calcium is removed by the addition of EDTA solution.

3. Interferences

3.1. There are no interferences in normal waters; however, heavy metals interfere depending on the amount present - about 0.5 mg/l of any metal or a combination of 2 or more metals will produce indistinct end-points. If an indistinct end-point is observed in the titration, the calcium should be determined by atomic absorption spectrophotometry as described elsewhere in this manual.

4. Sampling Procedure and Storage

4.1. The sample container (glass or plastic) should be tightly capped as soon as the sample has been collected and the calcium determined as soon as possible.

5. Sample Preparation

5.1. The sample aliquot used for analysis should be free from turbidity or filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Magnetic stirrer and stirring bars.

6.2. 10-ml microburette.

7. Reagents

7.1. Sodium hydroxide, IN: Dissolve 40 g sodium hydroxide pellets, NaOH, and make up to 1 litre with distilled water.

7.2. CalVer 11 indicator powder: Available from Hach Chemical Co., Ames, Iowa, Cat. No. 281.

7.3. Standard calcium solution, 1000 mg/l $CaCO_3$ or 400 mg/l Ca: Dry several g of calcium carbonate, $CaCO_3$, powder at 105°C overnight. Weigh 1.000 g into a 500-ml Erlenmeyer flask. Place a funnel in the neck of the flask and add 1 + 1 HCl, a little at a time, until all the $CaCO_3$ has dissolved. Add 200 ml distilled water and boil for a few min. to expel carbon dioxide. Cool, add a few drops of methyl red and adjust to an intermediate orange colour by adding 3N NH_4OH or 1 + 1 HCl as required. Transfer quantitatively to a 1-litre flask and make up to the mark with distilled water.

7.4. Standard Magnesium solution, 4116 mg/l $CaCO_3$ or 1000 mg/l Mg: Weigh out 1.000 g rough turnings of pure magnesium metal. Transfer quantitatively to a 500-ml Erlenmeyer flask. Place a funnel in the neck of the flask and add about 150 ml distilled water. Add 5.0 ml 1 + 1 H_2SO_4, 1 ml at a time. Mix well after each addition and allow the reactions to subside before adding more acid. After all the acid has been added and the reaction subsides, boil the contents of the flask for about 10 min. to ensure complete solution. Cool and transfer to 1 litre flask and make up to the mark with distilled water.

7.5. Standard EDTA solution: Analytical reagent grade disodium ethylene-diamine tetraacetate dihydrate, also called (ethylenedinitrilo) tetraacetic acid disodium salt (EDTA), is used. Weigh 11.169 g of the reagent, dissolve in distilled water, filter through Whatman No. 12 fluted paper and dilute to 3 litres. Check the titer by standardizing against standard calcium solution as follows:

7.5.1. Standardization of EDTA

A single solution for standardizing can be prepared by dilution of the prepared Ca and Mg standards to give a concentration of 200 mg/l Ca and 50 mg/l Mg. This solution is used for standardization because it contains Ca and Mg ions in a ratio found in many waters. One ml of this solution contains 0.2 mg Ca + 0.05 mg Mg or 0.7058 mg expressed as $CaCO_3$. Dilute three 10-ml aliquots of this standard to about 50 ml and titrate the separate aliquots for Ca following the procedure (8).

Mg/l Ca = Factor x ml EDTA

Factor obtained as follows: 1 ml standard = 0.2 mg Ca. If, for example, the average titration for 3 determinations was 5.25 ml using 10 ml of standard

5.25 ml EDTA = 2.0 mg Ca
1 ml EDTA = 0.381 mg Ca

and Factor (F) = $\frac{0.381 \times 1000}{\text{ml sample}}$

8. Procedure

8.1. Pipette a sample aliquot into a 150-ml beaker. The sample size should be such that not more than 10 ml of EDTA is used for titration.

8.2. Add 1.0 ml of NaOH solution (7.1).

8.3. Add 0.1 g (Hach Chemical Co. Measuring Spoon #511 is convenient) of CalVer 11 and titrate to the most intense blue end-point with EDTA.

9. Calculations

9.1. Calculate the concentration of calcium in the sample as follows:

Mg/l Ca = F x ml EDTA

where F is obtained from standardization of EDTA, see 7.5.1.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at calcium levels of 13 and 45 mg/l Ca were ±2.9% and 0.5% respectively.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

CARBON: ORGANIC, TOTAL AND DISSOLVED

(Infrared Analysis)

1. Scope and Application

1.1. This method is applicable to the determination of organic carbon in surface waters, wastes, and saline waters in the range 1 to 100 mg/l C. Higher values may be obtained by appropriate dilution of an aliquot.

2. Principle of Method

2.1. Single channel instrument.

2.1.1. A small, accurately measured volume of sample is injected into the combustion tube of a carbon analyzer with a hypodermic syringe. The combustion tube is kept at 950°C and receives a continuous stream of oxygen. Cobalt oxide impregnated asbestos packing is in the combustion tube and serves to disperse the sample and catalyzes oxidation. The carbonaceous material in the sample is oxidized, yielding carbon dioxide and steam. The carbon dioxide and steam are carried out of the furnace where the steam is condensed and removed. The carbon dioxide is swept into an infrared analyzer and a recorder then registers a signal that is proportional to the concentration of carbon dioxide in the oxygen stream, and, therefore, to the carbon content of the sample.

2.1.2. Inorganic carbonates (carbonate and bicarbonate) should be removed prior to analysis using the single channel instrument in order to obtain the organic carbon content of a sample.

2.2. Dual channel instruments.

2.2.1. The dual channel instrument is similar to the single channel instrument except it utilizes a second operation. In the second operation, a similar-sized sample is also syringe-injected into a flowing stream of air and swept into the second combustion tube which contains quartz chips wetted with 85 per cent phosphoric acid. This tube is enclosed in an electric heater thermostated at 150°C, which is below the temperature at which organic matter would be oxidized. The acid-treated packing causes the release of carbon dioxide from inorganic carbonates and the water is vaporized. The air flow carries the steam and carbon dioxide out of the furnace where the steam is condensed and removed. The carbon dioxide is measured in an infrared analyzer as in the single channel instrument. Subtracting the results in the second operation from the results obtained in the first operation yields an analysis of organic carbon.

3. Interferences

3.1. The samples must be homogeneous and be suitable for reproducible injections into the apparatus by means of a microlitre type syringe. It has been observed in laboratories of the Water Quality Division that the results of analyses on many samples for total organic carbon

using a blended sample are difficult to reproduce. This is thought due to the use of the small syringe for sample taking and its inability to withdraw identical samples. Consequently, a filtered (0.45 u) portion is used on such samples and the results termed "dissolved organic carbon".

3.2. There are no known serious interferences other than large particles in the sample that are not homogenized by blending.

4. Sampling Procedure and Storage

4.1. The sample should be refrigerated for storage and kept tightly capped.

5. Sample Preparation

5.1. Single channel instrument.

5.1.1. Total organic carbon: Blend a shaken sample for at least 5 minutes in a Waring blender and acidify to a pH of 2 or less with conc hydrochloric acid. Purge sample with CO_2 - free nitrogen gas for 5-10 min. or let stand for several hours to remove inorganic carbonates.

5.1.2. Dissolved organic carbon: Filter (0.45 u) a suitable sample aliquot and acidify to a pH of 2 or less with conc hydrochloric acid. Again remove inorganic carbonates as explained above (5.1.1)

5.2. Dual channel instruments.

5.2.1. Same as for single channel instrument only sample is not acidified.

6. Apparatus

6.1. Hypodermic Syringe, Hamilton no. 705 NLT microlitre (0-50 ul) syringe or equivalent.

6.2. Beckman Carbonaceous Analyzer, single or dual channel.

6.3. Waring blender or equivalent.

7. Reagents

7.1. Distilled water: The distilled water used in the preparation of standards and dilution of samples should be of the highest quality in order to have a small blank.

7.2. Organic carbon, stock solution, 1000 mg/l C: Dissolve 2.125 g anhydrous potassium biphthalate, $KHC_8H_4O_4$, in distilled water and dilute to 1 litre in a volumetric flask.

7.3. Organic carbon, standard solutions: Prepare standard solutions from the stock solution (7.2) as required.

7.4. Inorganic carbon, stock solution, 1000 mg/l C: Dissolve 3.500 g sodium bicarbonate, $NaHCO_3$, and 4.418 g sodium carbonate, Na_2CO_3, in distilled water in one-litre volumetric flask and make up to the mark.

7.5. Inorganic carbon, standard solution: Prepare standards from the stock solution (7.4) as required.

7.6. Packing for total carbon tube: Dissolve 20 g cobalt nitrate, $Co(NO_3)_2.6H_2O$, in 50 ml distilled water. Add this solution to 15 g long-fiber asbestos in a porcelain evaporating dish. Mix and evaporate to dryness on a steam bath. Place the dish in a cold muffle and bring to 950°C. After one to two hours at this temperature, remove the dish and allow to cool. Break up any large lumps and mix adequately but not excessively. With the combustion tube held in a vertical position, taper joint up, put about 1/2-inch of untreated asbestos in the tube first, then transfer in small amounts, approximately one gram of catalyst into the tube with forceps or tweezers. As it is added, tap or push the material gently with a 1/4-inch glass rod. Do not force the packing. The weight of the rod itself is sufficient to compress the material. When completed, the length of the packing should be about five or six centimeters. Test the packed tube by measuring the flow rate of gas through it at room temperature, and then at 750°C. The rate should not drop more than 20%.

7.7. Packing for carbonate tube, (dual channel instrument): Place a small wad of quartz wool or asbestos near the exit end of the carbonate evolution tube. From the entrance end add 6-12 mesh quartz chips, allowing these to collect against the wad to a length of 10 cm. Pour an excess of 85 percent phosphoric acid, H_3PO_4, into the tube while holding it vertically, and allow the excess to drain out.

8. Procedure

8.1. Instrument Adjustment

8.1.1. Turn on the infrared analyzer, recorder, and tube furnaces, setting the total carbon furnace at 950°C and the carbonate furnace at 175°C. Allow sufficient warm-up time for stable drift free operation; about 2 hours is required. If used daily the analyzer can be left on continuously. Adjust the oxygen flow rate to 80 - 100 ml/min. through the total carbon tube. Adjust the amplifier gain so that a 20-ul sample of the 100 mg/litre organic carbon standard gives a peak height of approximately half the recorder scale. Other adjustments may be used such as setting a 50 mg/litre standard at half the recorder scale. At these settings the noise level should be less than 0.5 percent of full scale.

8.1.2. Immediately prior to carrying out calibrations or analyses, inject several portions of the appropriate 100 mg/litre or 50 mg/litre standard into the tube to be used, until constant readings are obtained.

8.2. Analysis, Dual Channel Instrument.

8.2.1. Successively introduce 20 ul of each organic carbon standard (including a blank) and samples (see 5. Sample Preparation) into the total

carbon tube and record peak heights. Between injections allow the recorder pen to return to its base line. The actual injection technique is as follows: Rinse the syringe several times with the solution to be analyzed; fill, and adjust to 20 ul. Wipe off the excess with soft paper tissue, taking care that no lint adheres to the needle. Remove the plug from the syringe holder, insert the sample syringe, and inject the sample into the combustion tube with a single, rapid movement of the thumb. Leave the syringe in the holder until the flow rate returns to normal, then replace it with the plug.

8.2.2. In the same way, prepare a series of diluted carbonate standards containing 20,50,60,80, and 100 mg of inorganic carbon per litre. Turn the four-way valve of the apparatus to direct the gas flow through the low temperature tube and to the analyzer. Adjust the flow rate to 80 - 100 ml/min. and allow the baseline to become stabilized. Successively introduce 20 ul of each standard and sample, and a water blank into the low temperature tube and record peak heights.

8.3. Analysis, Single Channel Instrument.

8.3.1. Using the same technique outlined for the Dual-Channel Instrument (8.2.1.), inject sample (see 5. Sample Preparation) and standards and record peak heights.

9. Calculations

9.1. Dual Channel Instrument

9.1.1. Prepare calibration curves derived from the peak heights obtained with the standard total carbon and inorganic carbon solutions.

9.1.2. Determine the concentration of total carbon and inorganic carbon in the sample by comparing sample peak height with the calibration curves.

9.1.3. Determine the concentration of total organic carbon in the sample by subtracting the inorganic carbon value from the total carbon value.

9.2. Single Channel Instrument

9.2.1. Prepare a calibration curve derived from the peak heights obtained with the standard total carbon solutions.

9.2.2. Determine the concentration of organic carbon in the sample by comparing sample peak height with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division) the coefficients of variation at total organic carbon levels of 20 and 30 mg/l C were ±3.08% and ±0.02% respectively, using a single channel instrument.

11. References

11.1. Federal Water Pollution Administration, 1969. FWPCA Methods For Chemical Analysis of Water and Wastes, U.S. Department of the Interior, Cincinnati, Ohio.

11.2. Beckman Instructions. Laboratory Carbonaceous Analyzer 137879.

CHLORIDE

(Automated Thiocyanate Method)

1. Scope and Application

1.1. This method can be applied to natural waters and waste waters with a chloride content in the range of 0.1 to 100 mg/l. Higher concentrations can be brought within this range by proper dilution.

2. Principle of Method

2.1. The method is based on the displacement of thiocyanate ion (SCN) from mercuric thiocyanate by chloride ion and the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the coloured complex, ferric thiocyanate. This complex is proportional to the original chloride concentration and is measured in a colourimeter at 480 mu.

3. Interferences

3.1. There are no significant interferences.

4. Sampling Procedure and Storage

4.1. No special precautions.

5. Sample Preparation

5.1. The sample aliquot should either be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler II.

6.1.2. Manifold.

6.1.3. Proportioning Pump.

6.1.4. Colourimeter equipped with a 15-mm flow cell and 480-mu filters.

6.1.5. Recorder.

7. Reagents

7.1. Mercuric thiocyanate, saturated solution: Place 1 litre distilled water in a two-litre Erlenmeyer flask. Add 2 to 3 g mercuric thiocyanate, $Hg(SCN)_2$, and stir contents for several hours with a mechanical

or magnetic stirrer; then allow to settle overnight. Filter the solution into an amber reagent bottle.

7.2. Ferric ammonium sulphate solution: In a 2-litre volumetric flask dissolve 100 g ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, in approximately 500 ml distilled water. Carefully add 760 ml conc nitric acid; mix thoroughly; then complete the volume to 2 litres with distilled water. Filter into an amber reagent bottle.

7.3. Chloride stock solution, 10,000 mg/l Cl: In a 1-litre volumetric flask dissolve 16.482 g pre-dried sodium chloride, NaCl, in distilled water. Complete the volume to the mark with distilled water.

7.4. Chloride intermediate solution, 1000 mg/l Cl: Dilute 100 ml chloride stock solution (7.3) to 1 litre with distilled water.

7.5. Chloride working solutions: Prepare a series of standards by diluting suitable aliquots of intermediate chloride solution to 1 litre with distilled water.

7.6. Blank reagents.

7.6.1. "Mercuric thiocyanate reagent" is replaced by distilled water.

7.6.2. "Ferric ammonium sulphate" solution is prepared without the ferrous ammonium sulphate.

8. Procedure

8.1. Run the samples and standards at 20 per hour using the manifold as shown in Figure 2.

8.2. If any samples contain a significant level of colour, a correction should be made by re-running these samples through the system with the blank reagents (7.6). (A decision as to what constitutes a significant level of colour can only be made on experience gained by re-running samples of doubtful level of colour).

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of chloride in the samples by comparing sample peak heights with the calibration curve.

9.3. If a sample has been re-run with "blank" reagents, the chloride level in the sample is determined by subtracting the "apparent" chloride level obtained with the blank reagents (as determined by the peak height and calibration curve) from the "chloride" level obtained with the sample and regular reagents.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division) the coefficient of variation at a chloride level of 20 mg/l Cl was ±0.5%.

11. Reference

11.1. Technicon Corp., Tarrytown, New York. AutoAnalyzer methodology, method N-5b, chloride.

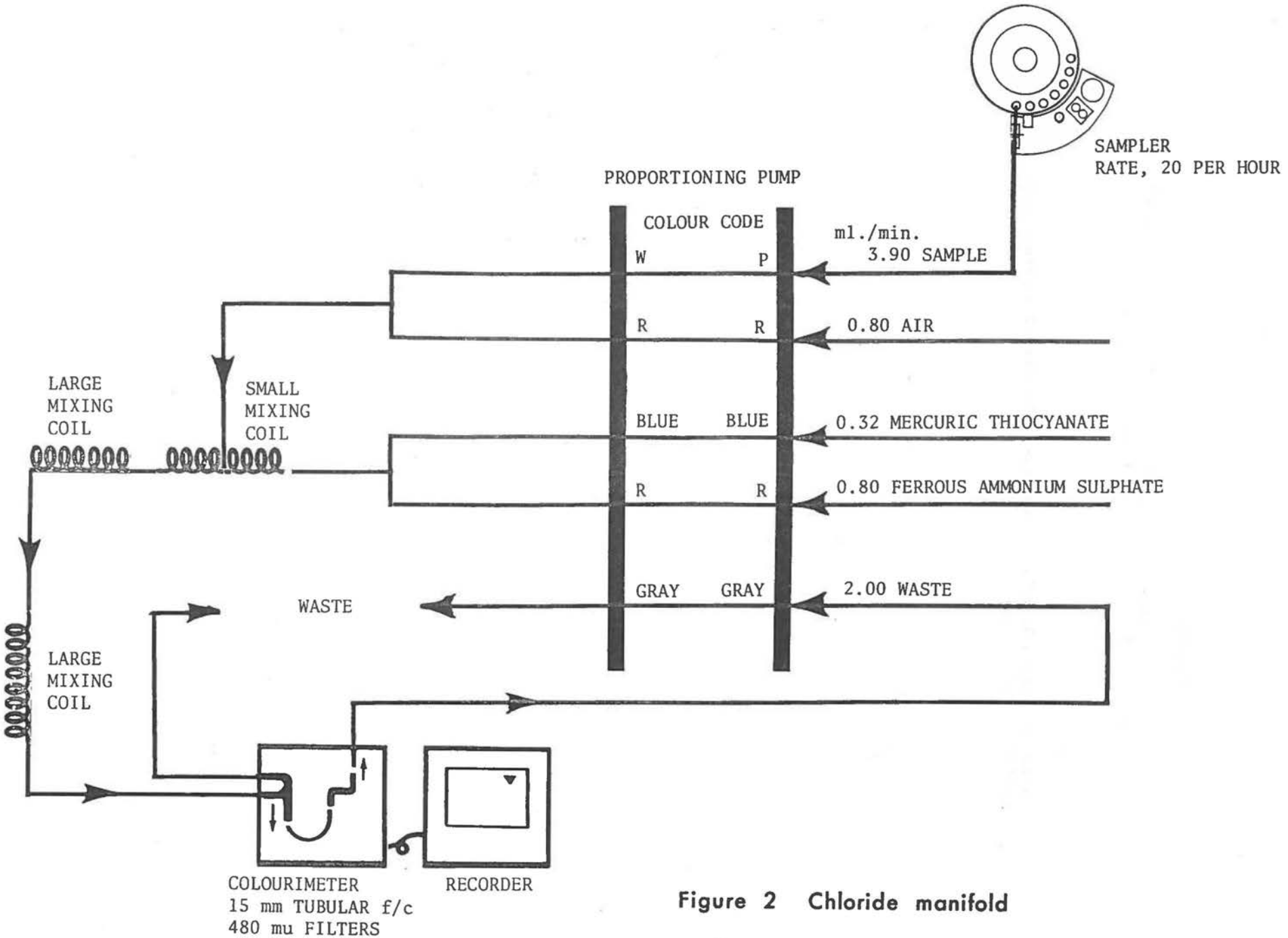

Figure 2 Chloride manifold

COLOUR

(Visual Comparison Method)

1. Scope and Application

1.1. This method is applicable to waters having colour derived from natural substances, i.e., leaves, barks, roots, humus and peat material. The method is not applicable to waters having colours derived from industrial wastes.

2. Principle of Method

2.1. The colour in a sample is determined by visual comparison with known concentrations of coloured solutions that are sealed in glass disks (Hellige Aqua Tester) or the sample colour is measured by visual comparison with platinum-cobalt standards.

2.2. One unit of colour is that produced by 1 mg/l platinum, in the form of chloroplatinate ion.

2.3. Definitions

2.3.1. Apparent colour includes the colour due to substances in solution and also that due to suspended matter.

2.3.2. True colour is the colour of the water from which the turbidity has been removed.

3. Interferences

3.1. Slight traces of turbidity interfere causing high results.

4. Sampling Procedure and Storage

4.1. The colour should be determined as soon as possible after collecting the sample and after opening the sample container in the laboratory as biological changes occurring may affect the colour.

5. Sample Preparation

5.1. If turbidity is present the sample should be centrifuged before measurement of the colour.

5.2. Filtration cannot be used because it may remove some of the colour as well as turbidity.

6. Apparatus

6.1. Hellige Aqua Tester Model 611A or equivalent.

6.2. Nessler Tubes, matched, 50 ml, tall form.

6.3. Centrifuge.

7. Reagents

7.1. Stock chloroplatinate solution, 500 units of colour: Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6 (equivalent to 0.500 g metallic platinum) and 1 g crystalized cobaltous chloride, $CoCl_2.6H_2O$ in distilled water containing 100 ml conc HCl and dilute to 1 litre with distilled water.

7.2. Standard colour solutions: Prepare standards having colours in the range 5 to 70 by appropriate dilutions of the stock solution (7.1). The following are suggested:

ml of Stock Solution Diluted to 50.0 ml with Distilled Water	Colour
0.0	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
3.5	35
4.0	40
4.5	45
5.0	50
6.0	60
7.0	70

8. Procedure

8.1. Apparent colour.

8.1.1. Observe the colour of the sample by filling a matched nessler tube to the 50-ml mark with the sample and comparing it with the standards. Look vertically downward through the tubes toward a white surface placed at such an angle that light is reflected upward through the columns of liquid. If turbidity has not been removed by centrifuging, the result is called "apparent colour".

8.1.2. If a Hellige Aqua Tester is used, fill the sample tube with the water sample and compare its colour against the colour standards in the Tester. Again, if turbidity has not been removed the result is "apparent colour".

8.2. True colour

8.2.1. To determine true colour, if turbidity is present, centrifuge the sample until the supernatant is clear. If clear, the sample is then compared with the standards either in the nessler tubes or using the Aqua Tester.

8.3. The coloured solutions supplied with the Aqua Tester should be periodically checked against the standard colour solutions to ensure reliability of results using the Tester.

9. Calculations

9.1. If the nessler tubes have been used, calculate the colour by means of the following equation:

$$\text{Colour units} = \frac{A \times 50}{B}$$

where A = estimated colour of diluted sample.
B = ml sample taken for dilution.

9.2. If the Aqua Tester was used the colour of the sample is read directly from the Tester after the sample has been matched with one of the standards. If the sample was diluted to bring it within the range of the Tester, apply the proper dilution factor to obtain the correct colour value.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at colour levels of 10 and 80 units was 0% using a Hellige Aqua Tester and recording the colour to the nearest 5 units.

11. References

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.2. Federal Water Pollution Control Administration, 1969. FWPCA methods for chemical analysis of water and wastes. Cincinnati, Ohio.

CYANIDE

1. Scope and Application

1.1. This method is applicable to the determination of cyanide in surface, wastes and sea water. Using the distillation assembly described the method is sensitive to about 2 ug/l.

2. Principle of Method

2.1. Distillation of the sample in the presence of sulphuric acid converts complex cyanides into hydrocyanic acid (HCN). The HCN gas is absorbed in a solution of sodium hydroxide and the cyanide determined colourimetrically.

2.2. In the colourimetric measurement, the cyanide in the sodium hydroxide solution after distillation is converted to cyanogen chloride, CNCl, by reaction with chloramine-T. The CNCl then forms a blue dye on the addition of pyridine - pyrazolone reagent and the absorbance measured at 620 mu.

3. Interferences

3.1. Sulphides interfere and should be removed prior to distillation, (see Section 5).

3.2. Other interfering substances are removed by distillation.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a 2-litre plastic bottle and analysed as soon as possible after collection.

4.2. Samples may be preserved by addition of sufficient NaOH to raise the pH to 11.0 or above, and stored in a cool place.

5. Sample Preparation

5.1. Decant a sample aliquot for distillation.

5.2. Sulphide is removed by treating the alkaline sample at pH 11.0 with small increments of powdered lead carbonate. Black lead sulphide precipitates in samples containing sulphide. Repeat this operation until no more lead sulphide forms. Filter and rinse the precipitate, add the rinse water to the filtrate, and use an aliquot for analysis. Avoid a large excess of lead carbonate and a long period of contact in order to minimize complexing or occlusion of the cyanide with the precipitated material.

6. Apparatus

6.1. One 1000-ml, 3-necked flask fitted with ground-glass joints; to the three necks are fitted a thistle funnel which extends below the liquid level, an air sparging tube drawn to a fine tip, and a Friedericks condenser (see Figure 3).

6.2. One heating mantle.

6.3. One magnetic stirrer-plate and stirring bar.

6.4. One gas absorption column made from Pyrex tubing 22mm I.D., 450-mm long, filled with glass helices (1/8-inch I.D.) (see Figure 3).

6.5. One Technicon proportioning pump fitted with 8 pumping tubes 0.110-inch I.D.

6.6. One 100-ml graduated cylinder mounted with clamp on a retort stand so that its position can be adjusted.

6.7. Spectrophotometer for use at 620 mu, providing a light path of 1 cm.

7. Reagents

7.1. Sodium hydroxide solution, 1N: Dissolve 40 g sodium hydroxide, NaOH, in 1 litre distilled water.

7.2. Mercuric chloride solution: Dissolve 34 g mercuric chloride, $HgCl_2$, in 500 ml distilled water. (Caution: Toxic; take care to avoid ingestion.)

7.3. Magnesium chloride solution: Dissolve 51 g magnesium chloride, $MgCl_2.6H_2O$, in 100 ml distilled water.

7.4. Sulphuric acid, H_2SO_4, concentrated.

7.5. Sodium hydroxide solution, 0.2N: Dissolve 8 g sodium hydroxide, NaOH, in 1 litre distilled water.

7.6. Acetic acid, CH_3COOH, conc and 1 + 4.

7.7. Stock cyanide solution: Dissolve 2.51 g potassium cyanide, KCN, in 1 litre water. Standardize with 0.0192N silver nitrate. The solution loses strength gradually and must be rechecked every week. Approximate strength, 1 ml = 1 mg CN. (Caution: Toxic; take care to avoid ingestion.)

7.8. Standard cyanide solution: Dilute 10 ml stock cyanide solution to 1 litre with distilled water; mix, and make a second dilution of 10 ml to 100 ml; 1.00 ml = 1.0 ug CN. This solution must be prepared daily. (Caution: Toxic; take care to avoid ingestion.)

7.9. Chloramine-T solution: Dissolve 1 g in 100 ml water. Prepare daily.

7.10. 1-phenyl-3-methyl-5-pyrazolone solution: Prepare a saturated aqueous solution (approximately 0.5 g/100 ml) by adding the pyrazolone to water at approximately 75°C. Agitate occasionally as the solution cools to room temperature. If necessary, the pyrazolone (melting point 127° - 128°C) can be purified by recrystallization from ethyl alcohol. Usually this is not required.

7.11. Pyridine.

7.12. Bis-pyrazolone.

7.13. Mixed pyridine-pyrazolone reagent: Mix 125 ml of the filtered, saturated aqueous solution of pyrazolone with a filtered solution containing 0.025 g bis-pyrazolone dissolved in 25 ml pyridine. Several minutes of mixing is usually necessary to dissolve the bis-pyrazolone in pyridine. The mixed reagent develops a pink colour on standing, but if used within 24 hr, this does not affect the colour production with cyanide. Prepare daily.

8. Procedure

8.1. Procedure for distillation.

8.1.1. Close pinch clamp (see Figure 3).

8.1.2. Add about 80 ml of water to the graduated cylinder and adjust the position of the cylinder so that the tube dips near the bottom of the cylinder.

8.1.3. Add 750 ml sample to the flask; add stirring bar, and start the stirrer.

8.1.4. Add 50 ml 1N NaOH solution (7.1) to the 250-ml beaker and start the pump.

8.1.5. When the absorption column is wet with NaOH solution, add 20 ml mercuric chloride solution (7.2) and 10 ml magnesium chloride solution (7.3) through the thistle tube.

8.1.6. Slowly add 37 ml concentrated sulphuric acid to the flask through the thistle tube.

8.1.7. Turn on the heating mantle and allow the contents of the flask to boil vigorously (Excess air as the flask heats up will escape from the equipment through the dip tube in the graduated cylinder).

8.1.8. After one hour of boiling, turn off the heating mantle and open pinch clamp.

8.1.9. Remove the tube pumping NaOH from the NaOH solution; rinse the content of the column into the NaOH beaker by pumping approximately 150 ml distilled water through the absorption column and collect in the NaOH beaker.

8.1.10. Transfer quantitatively to a 250-ml volumetric flask and make up to the mark.

8.2. Procedure for colourimetric measurement.

8.2.1. Transfer 15 ml of distillate to a 50-ml beaker

8.2.2. To prepare standard solutions for the calibration curve, use cyanide standard 1 ml = 1 ug CN. Pipette 0.0 (Blank), 0.2, 0.5, 0.8 and 1.0 ml into 50-ml beakers and make up to 15 ml with NaOH, 0.2N, (7.5). Proceed with 8.2.3 treating samples and standards the same.

8.2.3. Adjust pH to 6-7 with 1 + 4 acetic acid. Transfer to 25-ml volumetric flask.

8.2.4. Add 0.2 ml chloramine-T solution (7.9) and mix. Allow 1-2 min. for the reaction.

8.2.5. Add 5.0 ml mixed pyridine-pyrazolone reagent (7.13) and make up to the mark; mix. Allow 20 min. for colour development.

8.2.6. Read absorbance at 620 mu in a 1-cm cell.

8.2.7. As a check on the distillation step, periodically process cyanide standards solutions through the complete procedure.

9. Calculations

9.1. Calculate the cyanide concentration as follows:

$$CN,\ mg/l = \frac{F \times D}{C \times E}$$

where F = micrograms of cyanide determined
D = milliliters of diluted absorbing solution
C = milliliters of original sample
E = milliliters of aliquot used

10. Precision and Accuracy

10.1. No data available.

11. References

11.1. Goulden, P.D. Unpublished information on distillation set up. Water Quality Division, Ottawa, Ontario.

11.2. American Society for Testing and Materials, 1966. Book of ASTM Standards Part 23: Industrial Water; Atmospheric Analysis, Philadelphia.

11.3. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

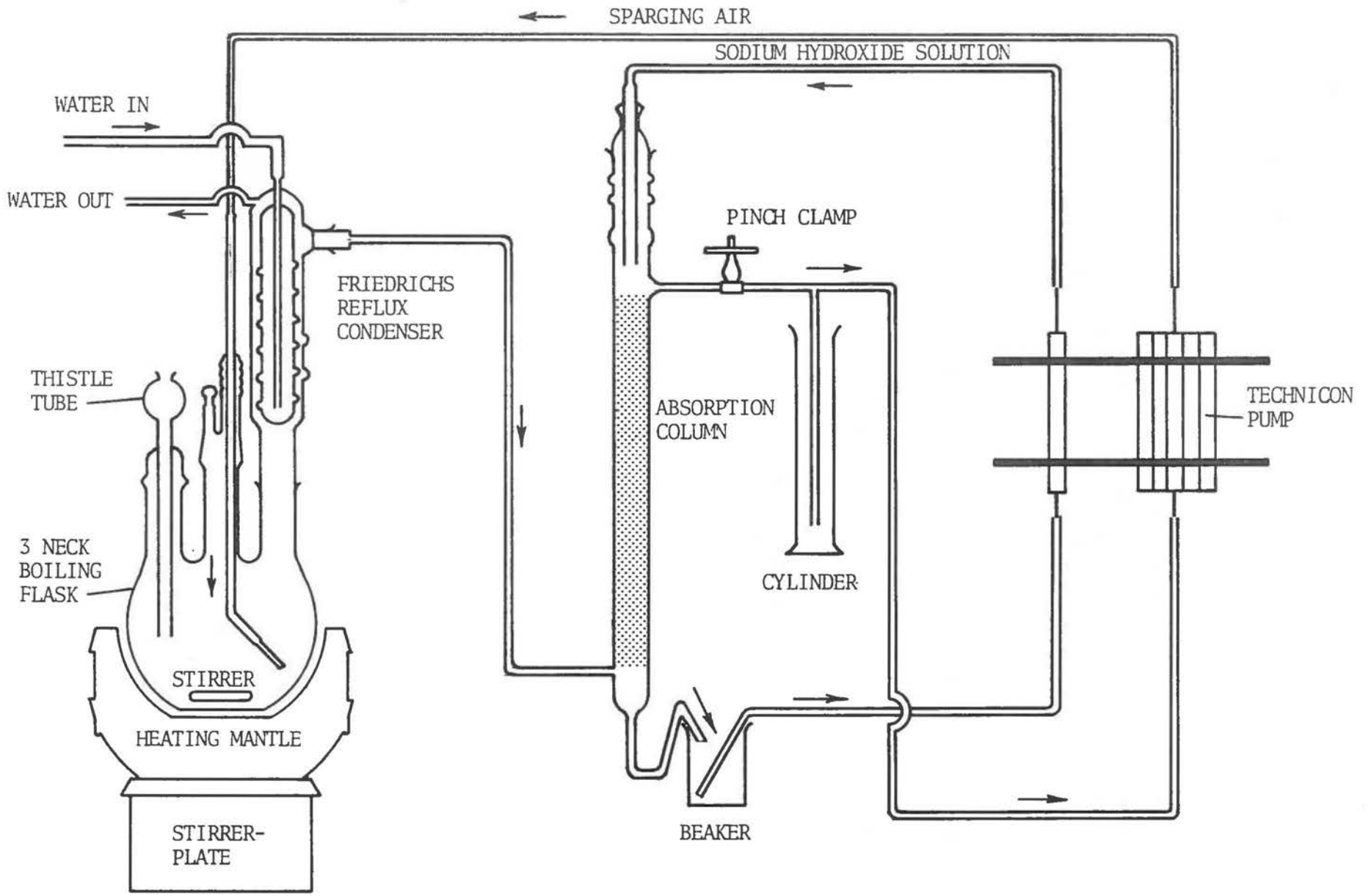

Figure 3 Cyanide distillation apparatus

FLUORIDE

(Specific Ion Electrode Method)

1. Scope and Application

1.1. This method is applicable to the determination of fluoride in all waters and wastes. All fluoride concentrations greater than 0.1 mg/l can be determined.

2. Principle of Method

2.1. Fluoride is determined potentiometrically using a specific ion fluoride electrode in conjunction with a standard reference electrode and a pH meter having an expanded scale capability. Specific ion meters are available that have a direct concentration scale for fluoride.

3. Interferences

3.1. There are no known significant interferences.

4. Sampling Procedure and Storage

4.1. The plastic sample container should be tightly closed immediately after collection and the concentration of fluoride ions should be determined as soon as possible thereafter.

5. Sample Preparation

5.1. No special preparation.

6. Apparatus

6.1. pH meter with expanded scale or fluoride specific ion meter: Corning model 12 pH meter or Orion model 801 specific ion meter, or equivalent of either instrument.

6.2. Fluoride Specific Ion Electrode (Orion No. 94-09).

6.3. Reference Electrode (Saturated calomel-sleeve-type).

6.4. Magnetic Stirrer (teflon-coated magnetic stirring bar).

7. Reagents

7.1. Total ionic strength adjustment buffer, TISAB: Prepare as follows:

7.1.1. To 57 ml glacial acetic acid, CH_3COOH, add 58 g sodium chloride, NaCl, and 1 g CDTA (cyclohexanediamine-tetra-acetic acid); dilute to 500 ml with distilled water. Adjust the solution to pH 5.8 with 5M sodium hydroxide solution and dilute to 1 litre.

7.2. Standardizing solutions.

7.2.1. Fluoride stock solution 100 mg/l F: Dissolve 0.2210 g anhydrous sodium fluoride, NaF, in distilled water and dilute to 1 litre.

7.2.2. Fluoride standard solutions: Prepare fluoride standard solutions by dilution of suitable aliquots of stock fluoride solution (7.2.1).

8. Procedure

8.1. Pipette 10.0 ml of water sample and standards (0.5, 1.0 and 2.0 mg/l F) into 50-ml beakers.

8.2. Pipette 10.0 ml of the TISAB solution into each beaker. Stir.

8.3. Procedure using an expanded-scale pH meter.

8.3.1. Calibrate electrodes and instrument. Set pH meter to the expanded mV position. Set the Temperature Compensator to the temperature of the sample being measured. All samples, standards and electrodes must be at the same constant room temperature. Stir all solutions for about 2 min before measurement; continue constant stirring during measurement.

8.3.2. Place electrodes successively in each standardizing solution; wait until the reading becomes stable (2 minutes); record millivolt readings. Blot electrodes dry between measurement.

8.3.3. Determine sample. Place electrodes in the sample. Record millivolt reading (wait for stabilization).

8.3.4. Recalibrate. Check the value of the 1 mg/l standardizing solution after each determination and recalibrate electrodes and instrument if necessary.

8.4. Procedure using a Specific Ion Meter.

8.4.1. Place the electrodes in the 1 mg/l fluoride solution, and set the Specific Ion Meter to the "F^-" position. Adjust the Calibration Control knob to obtain a mid-scale reading on the upper-most meter scale. Remember all readings are divided by 100, so the mid-scale value is read as 1 mg/l.

8.4.2. Wipe both electrodes and repeat the procedure using the 0.5 mg/l standard. Turn the Temperature Compensator knob so that the upper meter scale reads 50 (0.5 mg/l). The Specific Ion Meter is now calibrated to read fluoride unknowns. Recheck the calibration three or four times a day.

8.4.3. Read the fluoride concentration of the unknown directly from the meter scale.

9. Calculations

9.1. Expanded-scale pH meter.

9.1.1. Prepare a calibration curve by plotting on semilogarithm graph paper, electrode potentials developed in the solutions (linear axis) versus fluoride concentration (log axis). Determine concentration of fluoride in sample by comparing reading with the calibration curve.

9.2. Specific Ion Meters.

9.2.1. The Specific Ion Meters read directly in mg/l fluoride.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at fluoride levels of 0.2 and 1.0 mg/l F were ±0.79% and ±0.93% respectively, using an expanded-scale pH meter.

11. References

11.1. Harwood, J.E. 1969. The Use of An Ion - Selective Electrode For Routine Fluoride Analyses On Water Samples, Water Research 3,273.

11.2. Orion Application Bulletin No. 5A, 1969.

HARDNESS, TOTAL

(EDTA Titration and Calculation)

1. Scope and Application

1.1. The titrimetric method is applicable to the determination of total hardness in surface, ground and sea waters. All hardness concentrations greater than 1 mg/l $CaCO_3$ can be measured by using an appropriate sample aliquot.

1.2. The determination of total hardness by calculation from the results of the calcium and magnesium determinations obtained from atomic absorption analyses can be used to determine extremely small levels of total hardness (less than 1 mg/l $CaCO_3$) as well as very high levels such as found in sea waters.

2. Principle of Method

2.1. The titration method depends on the ability of ethylenediamine tetraacetic acid or its sodium salts (abbreviated EDTA) to form stable un-ionized complexes with calcium and magnesium ions. When the dye, Eriochrome Black T, is added to a solution containing calcium and magnesium ions, a pink complex is formed. When the solution is then titrated with standard EDTA solution, which removes calcium and magnesium from the dye complex, the dye is then changed back to its original blue colour. In this way Eriochrome Black T is used to indicate the end point for the titration of calcium and magnesium together (total hardness).

2.2. In the calculation method, the calcium and magnesium are determined by atomic absorption spectrophotometry and the total hardness calculated using the values obtained.

3. Interferences

3.1. There are no interferences in the titration method in normal waters; however, heavy metals interfere depending on the amount present -- about 0.5 mg/l of any metal or a combination of two or more metals will produce indistinct end points. If an indistinct end point is observed in the titration, the calcium and magnesium should be determined by atomic absorption spectrophotometry (described elsewhere in this manual) and the total hardness calculated. (See Section 9, Calculations).

4. Sampling Procedure and Storage

4.1. The sample container (plastic or glass) should be tightly capped as soon as the sample has been collected.

5. Sample Preparation

5.1. The sample aliquot used for analysis should be free from turbidity or filtered through 0.45-micron membrane filter.

6. Apparatus

6.1. Magnetic stirrer and stirring bars.

6.2. 10-ml microburette.

7. Reagents

7.1. Buffer solution: Dissolve 67.7 g ammonium chloride, NH_4Cl, in 572 ml conc ammonium hydroxide; add 5.00 g magnesium salt of EDTA and dilute to 1 litre with distilled water.

7.2. Eriochrome Black T indicator solution: Mix 0.5 g dye with 4.5 g hydroxylamine hydrochloride, $NH_2OH.HCl$. Dissolve this mixture in 100 ml 95% ethyl or isopropyl alcohol.

7.3. Standard calcium solution, 1000 mg/l $CaCO_3$ or 400 mg/l Ca: Dry several g calcium carbonate powder, $CaCO_3$, at 105°C overnight. Weigh 1.000 g into a 500-ml Erlenmeyer flask. Place a funnel in the neck of the flask and add dilute HCl, a little at a time, until all the $CaCO_3$ has dissolved. Add 200 ml distilled water and boil for a few min. to expel CO_2. Cool; add a few drops of methyl red and adjust to an intermediate orange colour by adding 3N NH_4OH or 1 + 1 HCl. Transfer quantitatively to a 1-litre flask and make up to the mark with distilled water.

7.4. Standard Magnesium solution: 4116 mg/l $CaCO_3$ or 1000 mg/l Mg. Weigh out 1.000 g rough turnings of pure magnesium metal, Mg. Transfer quantitatively to a 500-ml Erlenmeyer flask. Place a funnel in the neck of the flask and add about 150 ml distilled water. Add 5.0 ml of 1 + 1 H_2SO_4, 1 ml at a time. Mix well after each addition and allow the reactions to subside before adding more acid. After all the acid has been added and the reaction subsides, boil the contents of the flask for about 10 min. to ensure complete solution. Cool and transfer quantitatively to a 1-litre flask and make up to the mark with distilled water.

7.5. Standard EDTA solution: Dissolve 11.169 g disodium ethylenediamine tetraacetate dihydrate in 3 litres of distilled water and standardize as follows:

7.5.1. Standardization of EDTA solution:

A single solution for standardizing can be prepared by dilution of the prepared Ca and Mg standards to give a concentration of 200 mg/l Ca and 50 mg/l Mg. This solution contains Ca and Mg ions in a ratio found in many waters. One ml of this solution contains 0.2 mg Ca + 0.05 mg Mg or 0.7058 mg $CaCO_3$. Dilute three 10-ml aliquots of

this standard to 50 ml and titrate the separate aliquots for total hardness following the description in Procedure (8).

mg/l Total Hardness ($CaCO_3$) = F x ml EDTA

where the Factor (F) is obtained as follows:

1 ml standard = 0.7058 mg $CaCO_3$

If, for example, the average titration for 3 determinations was 7.17 ml using 10-ml aliquots of standard, then

7.17 ml EDTA = 7.058 mg $CaCO_3$

1 ml EDTA = 0.984 mg $CaCO_3$ and

$$\text{Factor (F)} = \frac{0.984 \times 1000}{\text{ml sample}}$$

8. Procedure

8.1. Pipette a sample aliquot into a 150-ml beaker. The sample size should be such that not more than 10 ml EDTA is used for the titration.

8.2. Add 1-2 ml buffer solution to give a pH of 10.0-10.1. Usually 1 ml is sufficient.

8.3. Add 2 drops of indicator and, while the solution is being stirred, titrate with EDTA until the last reddish tinge disappears from the solution.

9. Calculations

9.1. Titration method.

9.1.1. Calculate the concentration of total hardness in the sample as follows:

mg/l Total Hardness ($CaCO_3$) = F x ml EDTA

where Factor (F) is obtained from standardization (7.5.1.).

9.2. Calculation Method

9.2.1. If the calcium and magnesium were determined by atomic absorption spectrophotometry, calculate the total hardness by multiplying the concentration of each cation by the proper factor to obtain equivalent calcium carbonate, and summing these $CaCO_3$ concentrations. If present in significant amounts, other hardness producing cations must be determined and included in the computation. To obtain the $CaCO_3$ equivalent (mg/l) of the following cations, multiply the concentration found (mg/l) by the factor shown.

Cation	Factor
Ca	2.497
Mg	4.116
Sr	1.142
Fe	1.792
Al	3.710
Zn	1.531
Mn	1.822

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at total hardness levels of 52.0 and 181 mg/l $CaCO_3$ were ±0.65% and ±0.66% respectively, using the titration method and ±3.60% and ±0.63% respectively, using the atomic absorption method for determining calcium and magnesium, and calculating the total hardness.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

IODIDE

(Colourimetric Ceric Method)

1. Scope and Application

1.1. This colourimetric method is applicable to the determination of free iodide ion in water supplies from both surface and ground sources in the range 0.5 to 10 ug/l I.

2. Principle of Method

2.1. Iodide ions catalyze the reduction of ceric ions by arsenious acid; the effect is proportional, but non linearly to the amount of iodide present. Owing to the rapidly fading colour, the loss of ceric ions cannot easily be followed photometrically. However, in this method, the reaction is stopped after a given time interval by the addition of ferrous ammonium sulphate; the resulting ferric ions, which are directly proportional to the remaining ceric ions, develop a colour complex with potassium thiocyanate that is relatively stable.

3. Interferences

3.1. Chloride ion interference in the original sample is eliminated by adding excess sodium chloride to give a maximum, stable, chloride ion concentration to sensitize the reaction.

4. Sampling Procedure and Storage

4.1. The sample container should be tightly capped immediately after sample collection. No special storage precautions are necessary prior to analysis.

5. Sample Preparation

5.1. The sample aliquot either should be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. A constant temperature water bath operating at 30° ±0.5°C.

6.2. A spectrophotometer, measuring absorbance at 510 or 525 mu; using 1-cm path length cells.

6.3. Test tubes of 2 x 15 cm size.

6.4. Stop-watch.

7. Reagents

The stock solutions should all be stored in tightly stoppered containers in a dark place.

7.1. Sodium chloride solution: Dissolve 200.0 g sodium chloride, NaCl, in distilled water and dilute to 1 litre. If an interfering amount of iodine is present, recrystallize the NaCl, using water-ethanol mixture.

7.2. Arsenious acid, 0.1N: Dissolve 4.946 g arsenious oxide, As_2O_3, in distilled water; add 0.2 ml conc H_2SO_4 and dilute to 500 ml.

7.3. Sulphuric acid, conc.

7.4. Ceric ammonium sulphate solution, 0.02N: Dissolve 13.38 g ceric ammonium sulphate, $Ce(NH_4)_4.(SO_4)_4.4H_2O$, in distilled water; add 44 ml conc H_2SO_4 and dilute to 1 litre.

7.5. Ferrous ammonium sulphate reagent: Dissolve 1.50 g ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, in 100 ml distilled water containing 0.6 ml conc H_2SO_4. This requires daily preparation.

7.6. Potassium thiocyanate solution: Dissolve 4.0 g potassium thiocyanate, KSCN, in 100 ml distilled water.

7.7. Stock iodide solution, 1.00 ml = 200 ug I: Dissolve 0.2616 g anhydrous potassium iodide, KI, in distilled water and dilute to 1 litre.

7.8. Intermediate iodide solution, 1.00 ml = 4.00 ug I: Dilute 20.00 ml stock solution to 1 litre with distilled water.

7.9. Standard iodide solution, 1.00 ml = 0.100 ug I: Dilute 25.00 ml intermediate iodide solution to 1 litre with distilled water.

7.10. Working iodide solution, 1.00 ml = 0.010 ug I: Dilute 100 ml standard iodide solution (7.9) to 1 litre with distilled water.

8. Procedure

8.1. Add 10.00-ml water sample, or aliquot made up to 10.00 ml with distilled water, to a 2 x 15-cm test tube.

8.2. Add reagents to the sample in the following order:

1.00 ml NaCl solution, 0.50 ml arsenious acid solution, and 0.50 ml conc H_2SO_4.

8.3. Place the reaction mixture and the ceric ammonium sulphate solution in the 30°C water bath and allow to come to temperature equilibrium.

8.4. Add 1.00 ml ceric ammonium sulphate solution; mix the contents of the test tube by inversion, and start the stop-watch to time the reaction.

8.5. After 15 ±0.1 min, remove the sample from the water bath and immediately add 1.00 ml ferrous ammonium sulphate reagent while mixing, whereupon the yellow ceric ion colour should dissappear.

8.6. Then while mixing, add 1.00 ml potassium thiocyanate solution. Replace the sample in the water bath.

8.7. Within 1 hr after the thiocyanate addition, read the red colour in the spectrophotometer. As the method depends on a reduction in colour, set the highest standard at 0.00 absorbance to adjust the spectrophotometer.

8.8. Treat standards containing 0.0, 0.02, 0.04, 0.06, 0.08 and .10 ug I per 10.00 ml of solution as in 8.1 to 8.7. Run with each set of samples to establish a calibration curve. While it is possible to run higher standards, it is within the range of the standards listed that most samples fall.

9. Calculations

9.1. Calculate the concentration of iodide in the sample by the following equation:

$$\text{mg/l I} = \frac{\text{ug I}}{\text{ml sample}}$$

10. Precision and Accuracy

10.1. The method is reported to be accurate to ±0.3 ug/l I. (Standard Methods).

11. References

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.2. Rozina, B. and M. Dubravcic, 1953. Microdetermination of Iodides by Arresting the Catalytic Reduction of Ceric Ions, Analyst, 78, 594.

IRON

(Automated TPTZ Colourimetric Method)

1. Scope and Application

1.1. The method is applicable for both surface, ground, and waste waters with iron levels in the range 1 to 100 ug/l Fe. Samples having higher concentrations can be measured by appropriate dilution of an aliquot or by slight modification of the method if many samples high in iron are to be determined.

2. Principle of Method

2.1. The reagent 2,4,6, - tripyridyl-s-triazine (TPTZ) reacts with ferrous iron giving the violet coloured ion Fe $(TPTZ)^{+2}_{2}$. Ferric ion is initially reduced to ferrous ion with hydroxylamine hydrochloride. The violet iron complex concentration is measured in a colourimeter at 588 mu.

3. Interferences

3.1. There are no known significant interferences in normal waters.

3.2. Some samples from acid mine drainage contain organic compounds that precipitate under the acid conditions of this test, thereby causing high results. These samples should be analysed for iron by atomic absorption spectrophotometry.

4. Sampling Procedure and Storage

4.1. Immediately after sample collection, the container should be tightly capped. Iron may be present as a soluble salt or possibly in combination with organic acids, contributing to the colour of the sample. Basic waters containing more than 1 mg/l ferrous iron in apparent solution soon precipitate red, colloidal ferric hydroxide through oxidation. Hence, most surface waters seldom contain more than 0.5 mg/l dissolved iron, unless this is present under acid conditions as a sulphate or chloride. Ground waters may contain quite large amounts of dissolved ferrous iron, e.g., as the bicarbonate. Consequently, sample analysis should be carried out as rapidly as possible after collection.

4.2. Refer to Section 4, Metals (Atomic Absorption Methods).

5. Sample Preparation

5.1. Refer to Section 5, Metals (Atomic Absorption Methods).

6. Apparatus

6.1. Technicon AutoAnalyzer unit consisting of:

6.1.1. Sampler.

6.1.2. Manifold.

6.1.3. Proportioning Pump

6.1.4. Colourimeter equipped with 50-mm flow cell and 588-mu filters.

6.1.5. Range expander.

6.1.6. Recorder.

7. Reagents

7.1. TPTZ solution: To 0.624 g 2,4,6 - tripyridyl-s-triazine, add a few drops of conc hydrochloric acid and a small amount of distilled water. Dilute to 2 litres and filter through a 0.45-micron membrane filter.

7.2. Hydroxylamine hydrochloride solution: 100 g hydroxylamine hydrochloride, $NH_2OH.HCl$, are dissolved in 900 ml distilled water and filtered.

7.3. Sodium acetate-acetic acid buffer solution: To 328 g sodium acetate, CH_3COONa, add 230 ml conc acetic acid, CH_3COOH, and dilute to 2 litres. Filter.

7.4. Hydrochloric acid solution, 1N: Dilute 83 ml conc hydrochloric acid, HCl, to 1 litre with distilled water.

7.5. Stock iron solution, 100 mg/l Fe: Weigh out 0.1000 g analytical grade iron wire previously cleaned with dilute hydrochloric acid. Dissolve the wire in 10 ml 6N H_2SO_4 and dilute to 1 litre with distilled water.

7.6. Standard iron solutions: From the stock iron solution, prepare working solutions to cover the expected range of the samples.

7.7. Blank reagents:

7.7.1. TPTZ solution: This solution is replaced by distilled water.

7.7.2. Other solutions: All other solutions are used as originally prepared.

8. Procedure

8.1. Run the standards and samples at 20 per hour using the manifold as shown in Figure 4.

8.2. Higher concentrations of iron may be determined by any one, or a combination of two or more, of the following techniques:

8.2.1. Replace colourimeter (50-mm flow cell) with a colourimeter equipped with a 15-mm flow cell.

8.2.2. Remove range expander.

8.2.3. Replace one of the two sample lines (see Figure 4) with a distilled water line.

8.2.4. Dilution of sample prior to loading on sample tray.

8.3. If any samples contain a significant level of colour, a correction should be made by re-running these samples through the system with the blank reagents (7.7). (A decision as to what constitutes a significant level of colour can only be made on experience gained by re-running samples with doubtful level of colour). The blanks are determined by replacing the TPTZ reagent line for a distilled water line, leaving the rest of the manifold intact, and re-running the samples.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of iron in the samples by comparing sample peak heights with the calibration curve.

9.3. If a sample has been re-run with "blank" reagents, the iron level in the sample is determined by subtracting the "apparent" iron level obtained with the blank reagents (as determined by the peak height and calibration curve) from the "iron" level obtained with the sample and regular reagents.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a level of 50 mg/l Fe was ±0.7%

11. References

11.1. Collins, P.F., H. Diehl and G.F. Smith, 1959. "2,4,6 - tripyridyl-s-triazine as a Reagent for Iron. Determination of Iron, in Limestone, Silicates and Refractories", Analytical Chemistry, 31, (11), pp. 1862-67.

11.2. Technicon Instruments Corp. 1962. AutoAnalyzer Methodology Bulletin 11C.

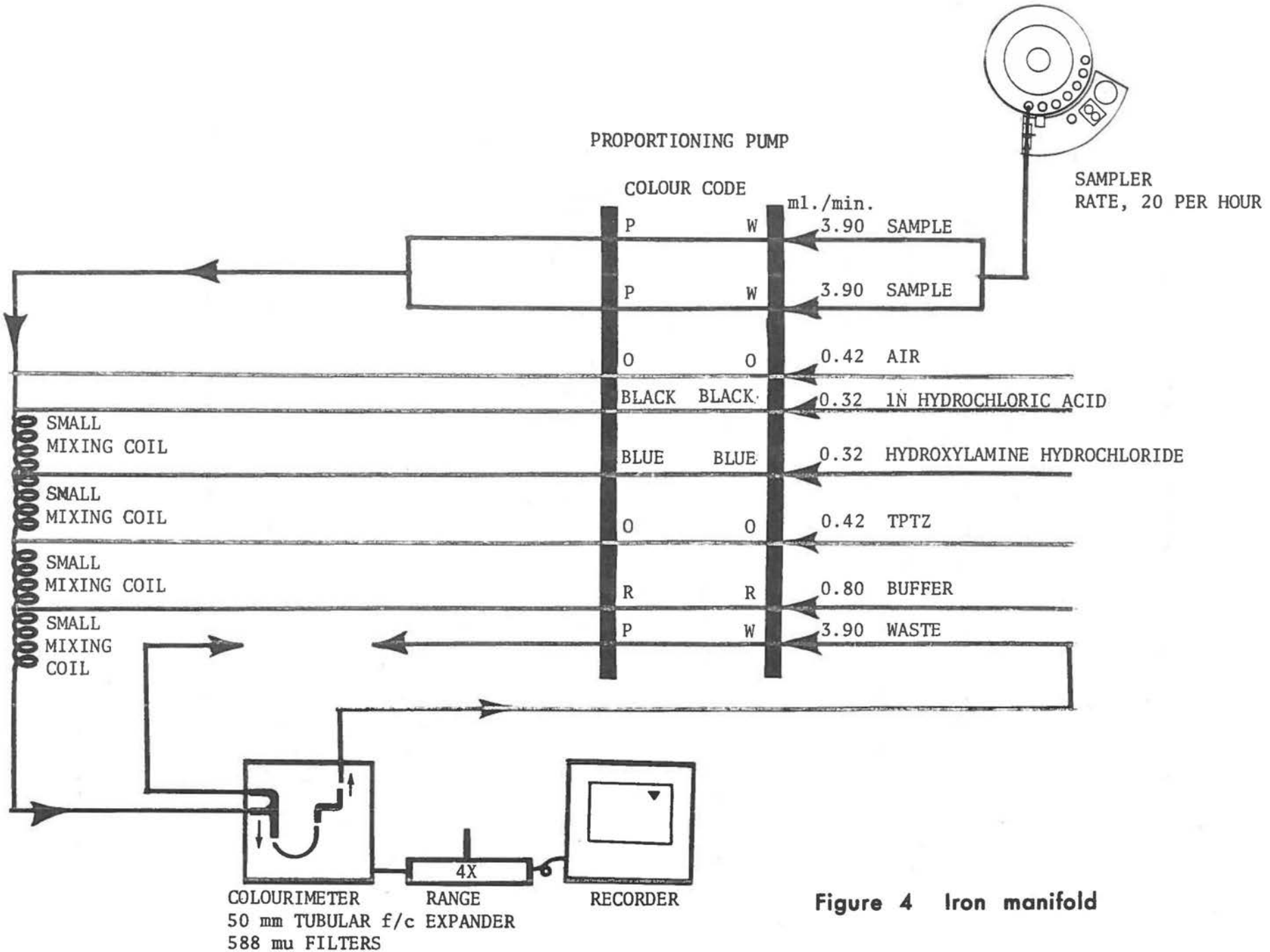

Figure 4 Iron manifold

MANGANESE

(Spot Test)

1. Scope and Application

1.1. This method is applicable to the determination of manganese in surface and ground waters. It is limited for quantitative purposes to very low manganese levels, 0.02 mg/l and less; higher values, up to 0.1 mg/l, may be determined by dilution of sample. Hence, the method is essentially a screening test to identify those samples that require quantitative determination by the atomic absorption spectrophotometric method described elsewhere in this manual.

2. Principle of Method

2.1. Permanganate and manganese dioxide react with tetramethyldiaminodiphenylmethane (Arnold's base, tetrabase) to give an intensely blue oxidation product.

3. Interferences

3.1. Strong oxidizing agents such as persulphate, chromate and peroxide interfere; however, these are not present in normal waters.

4. Sampling Procedure and Storage

4.1. Refer to Section 4, Metals (Atomic Absorption Methods).

5. Sample Preparation

5.1. Refer to Section 5, Metals (Atomic Absorption Methods)

6. Apparatus

6.1. Test tubes, 1-cm diameter.

7. Reagents

7.1. Stock manganese solution, 100 mg/l Mn: Heat 0.5 g manganous sulphate, $MnSO_4.H_2O$, for 1 hr at 180°C. Dissolve 0.275 g in deionized water containing 1 ml conc H_2SO_4 and dilute to 1 litre.

7.2. Standard manganese solutions: Prepare standard manganese solutions 0.02, 0.01 and 0.005 mg/l by suitable dilution of the stock manganese solution (7.1).

7.3. Ammonium hydroxide solution, 0.5%: Mix 1.0 ml conc ammonium hydroxide, NH_4OH, with deionized water and dilute to 200 ml.

7.4. Sodium acetate buffer, pH 4.8: Dissolve 10 g sodium acetate, CH_3COONa, in approximately 75 ml deionized water. Add 3.0 ml glacial acetic acid, CH_3COOH, and dilute to 100 ml.

7.5. Tetrabase solution: Dissolve approximately 10 mg tetramethyldiaminodiphenylmethane in 100 ml acetone. This solution is stable for about 2 weeks.

7.6. Potassium periodate, KIO_4, saturated solution: Prepare by adding an excess of KIO_4 in 200 ml deionized water.

8. Procedure

8.1. Pipette 1.0 ml sample into a test tube.

8.2. Pipette 1.0 ml blank (deionized water) and standard manganese solutions 0.02, 0.01, and 0.005 mg/l Mn.

8.3. Add 1 drop 0.5% NH_4OH (7.3).

8.4. Add 2 drops saturated KIO_4 solution (7.6), and mix.

8.5. Add 1 drop sodium acetate buffer (7.4). Mix, and let stand for at least 30 sec.

8.6. Add 1 drop tetrabase solution (7.5) and mix.

8.7. Immediately compare the colour of the sample with that of the standards. The colour is stable for only 2 or 3 min.

9. Calculations

9.1. The concentration of manganese in the sample is compared directly with the standards.

9.2. If a diluted sample is used, apply the proper dilution factor to obtain the manganese concentration in the original sample.

10. Precision and Accuracy

10.1. The method is accurate to ±0.005 mg/l of the actual manganese concentration in a sample, providing the sample contains less than 0.04 mg/l Mn.

11. Reference

11.1. United States Department of the Interior, 1960. Methods for Collection and Analyses of Water Samples. Geological Survey Water-Supply Paper 1454.

METALS

(Atomic Absorption Methods)

1. Scope and Application

1.1. Atomic absorption spectroscopy is used for the determination of metals in all types of water samples. This technique is used because of its ease of operation, sensitivity and applicability to a large number of metals in a wide variety of waters, i.e., surface, domestic, industrial waste and sea waters.

2. Principle of Method

2.1. Atomic absorption spectroscopy and flame emission photometry are similar in that a sample is aspirated into á flame and atomized. The major difference is in the fact that flame photometry measures the amount of light emitted, whereas in atomic absorption spectroscopy, a light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. The lamps used to furnish the light beam are called hollow cathode lamps and are made of or lined with the element of interest and filled with an inert gas, generally neon or argon. These lamps, when subjected to a current, emit the spectrum of the desired element together with that of the filler gas. Each element has its own characteristic absorption wavelength and, therefore, lamps composed of each element are employed. In atomic absorption spectroscopy, the element of interest in the sample is not excited, but is merely dissociated from its chemical bonds and placed into an unexcited, un-ionized "ground" state. The element is then capable of absorbing radiation from the light source. The amount of radiation absorbed in the flame is proportional to the concentration of the element present and this principle is the basis of atomic absorption spectroscopy.

2.2. Definition of Terms: Two terms frequently used in Atomic Absorption Spectrophotometry are sensitivity and detection limit. They are defined as follows:

2.2.1. Sensitivity: The concentration of a metal in milligrams per litre that produces an absorption of 1%.

2.2.2. Detection Limit: The concentration of a metal giving a signal equal to twice the variability of the background.

3. Interferences

3.1. General interferences experienced in atomic absorption spectroscopy are classified under three main categories - "Chemical", "Ionization" and "Matrix" interferences. Chemical interferences are generally caused by the inability of the flame to atomize the desired compound in the sample or the ability of the atoms thus produced to form some other compounds. This type of interference is normally experienced when the temperature of the flame is not sufficiently high to dissociate the desired compound from its chemical bonds. This type of interference

is mainly associated with solutions of alkaline-earth salts. For example - determination of barium, beryllium and calcium has poor sensitivity in air-acetylene flame. Use of a nitrous oxide-acetylene flame, which is much hotter, completely removes the chemical interference and improves the sensitivity of the system to detect the metal ions. However, too hot a flame causes another type of interference - ionization, which is caused when a large proportion of the atoms in the sample become ionized, thus causing them to absorb at a different radiation line. The degree of ionization generally depends upon burning conditions and the temperature of the flame. This interference is usually eliminated by introducing an excess of other metal ions in a flame which is more easily ionizable than the metal which is to be determined, e.g., the addition of an excess of potassium or lanthanum is recommended to reduce ionization of calcium and barium.

Matrix or bulk interference is caused by either a change in viscosity of the solution or by a large excess of extraneous ions. For example, the absorption of a given concentration of an element in organic solvents can be as much as four to five times higher than the aqueous solution of the same concentration aspirated into the flame. Many workers have also suggested matching the standards and samples with materials that are present in excess of 1%.

Chemical interferences may be removed by separating the metal from the interfering materials by solvent extraction techniques. These techniques serve not only to eliminate interferences but also to increase the sensitivity of the analysis.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a thoroughly cleaned polyethylene bottle. The treatment of the sample at the time of collection will determine the type of data obtained from the analysis, i.e., dissolved, total, etc. Refer to Sample Preparation (5) for explanation of measurements in order that the proper sampling technique will be used for the type of data required.

4.2. As some metals require special treatment for sampling and storage, consult individual method descriptions for special instructions.

5. Sample Preparation

5.1. Terminology of measurements according to sampling procedure or preparation of sample for analysis.

5.1.1. Dissolved: Samples used for analysis should be free from turbidity or filtered through a 0.45-micron membrane filter (previously well washed with dilute HNO_3 solution). The sample should be filtered at the time of collection, or, if this is not possible, as soon as it arrives in the laboratory. The sample should be acidified (2 ml conc HNO_3 per litre) after filtration.

5.1.2. Suspended: Sample is filtered through a 0.45-micron membrane filter (previously well washed with dilute HNO_3 solution) and the analysis carried out on the portion of the sample retained on the filter. (See 5.2 for details).

5.1.3. Total: Sum of the concentrations in the dissolved and suspended fractions. In general, the practice in the Water Quality Division is to treat the whole sample by transferring contents of sample container to a beaker and, by treatment, ensure dissolution of metals. (See 5.2 for details).

5.1.4. Extractable: Dissolved concentration plus the concentration of metal from the suspended solids (turbidity) that is dissolved by dilute mineral acid. The extractable metal content can be determined by analysis after adding mineral acid to the sample bottle (2 ml/litre), shaking the sample and allowing it to stand overnight. In many cases, this represents the total metal content if all sediment has dissolved.

5.2. Preparation of sample for analyses of Suspended (5.1.2) and Total (5.1.3) metal content.

5.2.1. For the determination of suspended metals a representative volume of sample is filtered through a 0.45-micron membrane filter (previously well washed with dilute HNO_3 solution) and the filter with its contents transferred to a 250-ml beaker; 3 ml of conc HNO_3 are added. The beaker is covered with a watch glass and heated gently. When the membrane has dissolved, increase the heat and evaporate to dryness. Cool, and add another 3 ml conc HNO_3; continue heating until digestion is complete (light coloured residue). Add 2 ml HCl (1 + 1) to the dry residue and warm gently to dissolve the material. Wash down the sides of the beaker with deionized water and, if necessary, filter to remove silicates and other insoluble materials that might clog the atomizer. Make up with deionized water to the volume of the original sample that was filtered.

5.2.2. For the determination of total metal content, the contents of the sample container (usually 4-oz sample containers are used for metal analyses) are transferred to a 250-ml beaker. Larger beakers are necessary if the sample containers are larger than 4 oz. To the sample in the beaker add 3 ml conc HNO_3 and evaporate to dryness on a hot plate. Cool, and add another 3 ml conc HNO_3, continue heating until digestion is complete (light coloured residue). Add 2 ml HCl (1 + 1) to the dry residue and warm gently to dissolve the material. Wash down the beaker with deionized water and filter if necessary. Make up with deionized water to the original volume of sample that was transferred to the beaker.

6. Apparatus

6.1. Atomic Absorption Spectrophotometer: Perkin-Elmer Model 303 or 403, or equivalent. Instrument settings described in this manual refer to the Perkin-Elmer 303 and 403 instruments only.

6.2. Hollow Cathode Lamps.

6.3. pH - meter.

6.4. Mechanical Shaker and holders for 250-ml volumetric flasks.

6.5. Glassware: All glassware such as Erlenmeyer flasks, beakers, pipettes, volumetric flasks and funnels should be rinsed with 1:1 nitric acid and then rinsed with deionized water.

6.6. Filtering apparatus.

7. Reagents

7.1. Deionized distilled water: Prepare by passing distilled water through a mixed-bed ion exchange resin.

7.2. Nitric acid, HNO_3, conc. Special grade for Atomic Absorption analysis.

7.3. Hydrochloric acid, HCl, conc. Special grade for Atomic Absorption analysis.

7.4. Stock metal solutions: Prepare as directed under individual metal descriptions.

7.5. Ammonium pyrrolidine dithiocarbonate (APDC) solution, 1%: Dissolve 1 g APDC in 100 ml deionized water. Prepare fresh before use.

7.6. Methyl isobutyl ketone (MIBK).

7.7. Buffer (pH 4.75) solution: Dissolve 272 g sodium acetate, CH_3COONa, in distilled water and dilute to about 1 litre in a 2-litre beaker. Add acetic acid, CH_3COOH, to the solution until a pH of 4.75 is reached (use a pH meter). Dilute to 2 litres. Extract this solution with 0.01% dithizone (7.8) until the extract remains green, then extract with carbon tetrachloride, CCl_4, to remove excess dithizone.

7.8. Dithizone 0.01%: Dissolve 0.01 g of diphenylthiocarbazone in 100 ml carbon tetrachloride.

8. Procedure

8.1. See individual methods for standard solutions, instrumental parameters and special techniques not normally used.

8.2. General procedure for direct aspiration.

8.2.1. The analyst should follow the manufacturer's operating instructions for his particular instrument. As a rule, the following steps are followed: The hollow cathode lamp is installed, the source current set according to the manufacturers recommendations and the lamp allowed to warm up for a period of time depending on the lamp used (usually 5-10 min. is sufficient). During this period, select the proper wavelength and slit width, light the flame and regulate the flow of fuel and oxidant; adjust the burner for maximum absorption and stability. Then aspirate each standard and sample and record readings.

8.3. General procedure for solvent extraction with APDC and MIBK. If the concentration of metal is not sufficient to determine by direct aspiration, or when the sample contains a large amount of dissolved solids, some metals may be chelated and extracted with organic solvents. The general procedure using APDC and MIBK is outlined below; other extraction procedures are detailed under the individual method descriptions.

8.3.1. Pipette a volume of sample (100 ml maximum) into a 250-ml volumetric flask and, if necessary, dilute to 100 ml with deionized water.

8.3.2. Prepare a blank and sufficient standards to cover the expected range of the sample.

8.3.3. Add 5.0 ml buffer (7.7) to each and mix by swirling flasks.

8.3.4. Add 5.0 ml APDC (7.5) to each and mix by swirling flasks.

8.3.5. Add 10.0 ml MIBK (7.6) and shake the flasks for 5.0 min on a mechanical shaker equipped with special holders for the flasks.

8.3.6. Allow the layers to separate and to each slowly add deionized water down the side of the flask to float the organic layer to the top of the flask.

8.3.7. Aspirate the ketone layer (See Note 1) and record readings for each standard and sample.

Note 1: Aspiration of an organic solvent into the flame: When working with organic solvents, reduce the fuel-to-air ratio because the burning of the organic solvent contributes to the fuel supply and, in addition to lifting the flame off the burner, may produce an undesirable luminescent flame. In setting the fuel-to-air ratio of the gas mixture at the burner, start with the settings recommended by the manufacturer for the analysis and gradually reduce the fuel flow (while the solvent is being aspirated) until the flame is similar to the flame before aspiration of the organic solvent. With the nitrous oxide burner, approximately double the flow of acetylene is required over that normally used for the air-acetylene burner and the acetylene should be adjusted until the flame is a rose-red.

8.3.8. If more sensitivity is required, it is possible to use more sample, e.g., 200 ml with the use of larger flasks (500 ml) for extraction. Also the reagents added should be proportionately increased.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of metal in the sample by comparing sample peak height with the calibration curve.

10. Precision and Accuracy

10.1. Consult individual method descriptions.

11. References

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ALUMINUM

1. Detection Limit

1.1. Direct aspiration, 1.0 mg/l.

1.2. Solvent extraction, 0.05 mg/l.

2. Reagents

2.1. Stock aluminum solution, 500 mg/l: Dissolve 8.792 g potassium aluminum sulphate, $K_2Al_2(SO_4)_2.24H_2O$, in distilled water and dilute to 1 litre in a volumetric flask.

2.2. Standard aluminum solutions: Prepare standards to cover the desired range by appropriate dilution of the stock solution (2.1).

2.3. 8-hydroxy-quinoline: Dissolve 20 g 8-hydroxy-quinoline, in IN acetic acid (60 ml glacial acetic acid per litre) and make up to 1 litre with the IN acid.

2.4. Buffer solution: Dissolve 200 g ammonium acetate, CH_3COONH_4, in distilled water containing 70 ml conc ammonium hydroxide, NH_4OH, and make up to 1 litre with distilled water.

2.5. Chloroform, $CHCl_3$.

3. Special Procedure for Low Concentrations of Aluminum

3.1. To 100-ml sample in a 250-ml separatory funnel add 2 ml 8-hydroxy quinoline (2.3) and 3 ml buffer solution (2.4). If necessary adjust to pH 8.0 ±0.5.

3.2. Add 5 ml chloroform, shake the separatory funnel vigourously and drain the extract into a test tube.

3.3. Repeat the extraction with a second 5 ml chloroform and combine with the extract from (3.2).

3.4. Determine aluminum in sample by comparison with standards which have been similarly extracted, using pure chloroform to establish a base line.

4. Instrument Parameters

4.1. Lamp: Aluminum.

4.2. Slit: 4.

4.3. Wavelength: 309.3 mu.

4.4. Burner: Nitrous Oxide.

4.5. Fuel: Acetylene.

4.6. Oxidant: Nitrous Oxide.

4.7. Type of Flame: Reducing.

ANTIMONY

1. Detection Limit

1.1. Direct aspiration: 0.2 mg/l Sb.

1.2. Solvent extraction: 0.0002 mg/l Sb (200-ml sample).

2. Stock Solution

2.1. Stock antimony solution, 1000 mg/l Sb: Dissolve 2.7426 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$, in deionized water, and dilute to 1 litre with deionized water.

3. Instrument Parameters

3.1. Lamp: Antimony.

3.2. Wavelength: 217.6.

3.3. Slit: 3.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

BARIUM

1. Detection Limit

1.1. Direct aspiration: 0.1 mg/l.

2. Reagents

2.1. Sodium chloride solution: Dissolve 250 g sodium chloride, NaCl, in distilled water and make up to 1 litre.

2.2. Stock barium solution, 1000 mg/l Ba: Dissolve 1.7787 g barium chloride, $BaCl_2.2H_2O$, in distilled water and dilute to 1 litre in a volumetric flask.

2.3. Standard barium solutions: Prepare standards to cover the desired range by appropriate dilution of the stock solution (2.2).

3. Procedure

3.1. To 100-ml sample and standards add 2.0 ml sodium chloride solution (2.1); mix, and aspirate sample and standards.

Note: The sodium chloride solution is added to overcome ionization interference in the flame.

3.2. Establish a base line using a solution of deionized water containing the sodium chloride solution (2.1) at a concentration of 2 ml for each 100 ml deionized water.

4. Instrument Parameters

4.1. Lamp: Barium.

4.2. Wavelength: 553.6 mu.

4.3. Slit: 3.

4.4. Burner: Nitrous Oxide.

4.5. Fuel: Acetylene.

4.6. Oxidant: Nitrous Oxide.

4.7. Type of Flame: Reducing.

BERYLLIUM

1. Detection Limit

1.1. Direct aspiration, 0.01 mg/l.

1.2. Solvent extraction, 0.001 mg/l.

2. Reagents

2.1. Stock beryllium solution 1000 mg/l Be: Dissolve 11.6586 beryllium sulphate, $BeSO_4$, in distilled water containing 2 ml conc HNO_3 and dilute to 1 litre in a volumetric flask.

2.2. Standard beryllium solutions: Prepare standards to cover the desired range by appropriate dilution of the stock solution (2.1).

2.3. 8-hydroxy-quinoline: Dissolve 20 g in IN acetic acid (60 ml glacial acetic acid per litre) and make up to 1 litre with the IN acid.

2.4. Buffer solution: Dissolve 200 g ammonium acetate, CH_3COONH_4, in distilled water containing 70 ml conc ammonium hydroxide, NH_4OH, and make up to 1 litre with distilled water.

2.5. Chloroform, $CHCl_3$.

3. Special Procedure for Low Concentrations of Beryllium

3.1. To 100-ml sample in a 250-ml separatory funnel add 2 ml 8-hydroxy quinoline (2.3) and 3 ml buffer solution (2.4). If necessary adjust to pH 8.0 ±0.5.

3.2. Add 5 ml chloroform, shake the separatory funnel vigourously and drain the extract into a test tube.

3.3. Repeat the extraction with a second 5 ml chloroform and combine with the extract from (3.2).

3.4. Determine beryllium in sample by comparison with standards which have been similarly extracted, using pure chloroform to establish a base line.

4. Instrument Parameters

4.1. Lamp: Beryllium.

4.2. Wavelength: 234.8 mu.

4.3. Slit: 5.

4.4. Burner: Nitrous Oxide.

4.5. Fuel: Acetylene.

4.6. Oxidant: Nitrous Oxide.

4.7. Type of Flame: Reducing.

CADMIUM

1. Detection Limit

1.1. Direct aspiration, 0.01 mg/l Cd.

1.2. Solvent extraction, 0.001 mg/l Cd (100-ml sample).

2. Stock Solution

2.1. Stock cadmium solution, 100 mg/l Cd: Weigh 0.100 g pure cadmium metal and dissolve in 5.0 ml conc HCl using heat to assist dissolution. Transfer quantitatively to a 1-litre volumetric flask and make up to volume with deionized water.

3. Instrument Parameters

3.1. Lamp: Cadmium.

3.2. Wavelength: 228.8 mu.

3.3. Slit: 4.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

4. Precision and Accuracy

4.1. In a single laboratory (Water Quality Division), the coefficient of variation at a cadmium level of 10 ug/l was ±3.5% using the solvent extraction method.

CALCIUM

1. Range and Detection Limit

1.1. Range: 0.1 - 80 mg/l Ca. The upper range can be extended by dilution of the original sample.

1.2. Detection Limit: 0.002 mg/l Ca.

2. Reagents

2.1. Lanthanum chloride solution (10% La): Weigh 117.2 g lanthanum oxide, La_2O_3, and transfer to a 1-litre beaker. Add about 600 ml deionized water followed by 200 ml conc hydrochloric acid. Heat the beaker and stir the mixture until the salt has dissolved. Cool, filter into a one-litre flask and make up to the mark with deionized water. Store in a polyethylene bottle.

2.2. Stock calcium solution, 400 mg/l Ca: Dry several g calcium carbonate, $CaCO_3$, powder at 105°C overnight. Weigh 1.000 g into a 500-ml Erlenmeyer flask. Place a funnel in the neck of the flask and add dilute HCl, a little at a time, until all $CaCO_3$ has dissolved. Add 200 ml distilled water and boil for a few min to expel CO_2. Cool, add a few drops of methyl red and adjust to an intermediate orange color by adding 3N NH_4OH or 1 + 1 HCl. Transfer quantitatively to a 1-litre flask and make up to the mark with distilled water.

2.3. Standard calcium solutions: Prepare a series of standard solutions from 0.0 to 80 mg/l by dilution of the stock calcium solution (2.2). To each 1000 ml of working solution prepared add 20.0 ml 10% lanthanum solution (2.1) to make a total volume of 1020 ml.

2.4. Blank solution: This solution is used to run the base line and is prepared by adding 20.0 ml lanthanum solution (2.1) to 1 litre deionized water.

3. Procedure

3.1. Pipette a 25-ml sample into a 50-ml Erlenmeyer flask.

3.2. To the sample add 0.5 ml lanthanum solution (2.1) and mix by swirling the flask.

3.3. Establish a baseline by aspirating the blank solution (2.4).

3.4. Aspirate standard calcium solutions and sample, and record readings. Calculate result as outlined in Calculations, 9 (See Metals).

4. Instrument Parameters

4.1. Lamp: Calcium-Magnesium

4.2. Wavelength: 422.7 mu.

4.3. Slit: 4.

4.4. Burner: 2 inch single slot placed crossways to light path.

4.5. Fuel: Acetylene.

4.6. Oxidant: Air.

4.7. Type of Flame: Reducing.

5. Precision and Accuracy

5.1. In a single laboratory (Water Quality Division), the coefficient of variation at a calcium level of 10 mg/l Ca was ±0.6%.

CHROMIUM (TOTAL)

1. Detection Limit

1.1. Direct aspiration: 0.01 mg/l Cr.

1.2. Solvent Extraction: 0.2 ug/l Cr.

2. Reagents

2.1. Buffer solution: Dissolve 100 g ammonium acetate, CH_3COONH_4, in deionized water and add 40 ml 1 + 3 ammonium hydroxide, NH_4OH. Complete the volume to 1 litre.

2.2. Bromine water: 1% solution.

2.3. Stock chromium solution, 50 mg/l Cr: Dissolve 0.1414 g anhydrous potassium dichromate, $K_2Cr_2O_7$, in distilled water and dilute to 1 litre.

2.4. APDC (See Metals 7.5).

2.5. Methyl isobutyl ketone (MIBK).

3. Procedure

3.1. Place a 100-ml sample that has been adjusted to a pH 1.6 (this will be the pH of most samples if they were preserved using 2 ml conc HNO_3 per litre of sample) in a 250-ml volumetric flask.

3.2. Prepare a series of chromium standards from 0.0 to 20 ug/l, adjust pH to 1.6 and place into 250-ml volumetric flasks. Add deionized water to a total volume of approximately 100 ml.

3.3. To each flask add 0.5 ml bromine water and warm on a water bath until the colour due to the bromine water has disappeared; then cool to room temperature.

3.4. Adjust the pH of the sample and standards to 3.5 using the buffer (normally 2.0 ml is required); mix.

3.5. Add 3.0 ml APDC to each and mix.

3.6. Add 5.0 ml MIBK to each and shake the flasks for 5.0 min on a mechanical shaker equipped with special holders for the flasks.

3.7. Allow the layers to separate and float the organic layer of each flask to the top by adding deionized water slowly down the side of the flask.

3.8. Aspirate the organic layer of each standard and sample, and record readings.

4. Instrument Parameters

4.1. Lamp: Chromium.

4.2. Wavelength: 358.0 mu.

4.3. Slit: 3.

4.4. Burner: 3 slot.

4.5. Fuel: Acetylene.

4.6. Oxidant: Air.

4.7. Type of Flame: Reducing (slightly yellow).

5. Precision and Accuracy

5.1. In a single laboratory, the coefficient of variation at a concentration of 10 ug/l was ±2.9%.

COBALT

1. Detection Limit

1.1. Direct Aspiration: 0.01 mg/l Co.

1.2. Solvent Extraction: 0.001 mg/l Co.

2. Stock Solution

2.1. Stock cobalt solution, 1000 mg/l Co: Dissolve 4.037 g cobaltous chloride, $CoCl_2.6H_2O$, in deionized water. Add 10 ml conc HNO_3 and dilute to 1 litre with deionized water.

3. Instrument Parameters

3.1. Lamp: Cobalt.

3.2. Wavelength: 240.7 mu.

3.3. Slit: 3.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

4. Precision and Accuracy

4.1. In a single laboratory (Water Quality Division), the coefficient of variation at a cobalt level of 10 ug/l Co was ±1.3% using the solvent extraction method.

COPPER

1. Detection Limit

1.1. Direct aspiration, 0.01 mg/l Cu.

1.2. Solvent extraction, 0.001 mg/l Cu.

2. Stock Solution

2.1. Stock copper solution, 1000 mg/l Cu: Weigh 1.000 g polished electrolytic copper wire, Cu, and transfer to 1-litre beaker. Add 10 ml 1 + 1 HNO_3 and a small amount of deionized water. After reaction has ceased, gently warm the contents of the beaker to complete solution of the wire. Cool, and transfer to a 1-litre volumetric flask and make up to volume with deionized water.

3. Instrument Parameters

3.1. Lamp: Copper.

3.2. Wavelength: 324.7 mu.

3.3. Slit: 4.

3.4. Burner:

3.4.1. Low temperature (direct aspiration).

3.4.2. 4 in single slot (solvent extraction).

3.5. Fuel:

3.5.1. Propane (direct aspiration).

3.5.2. Acetylene (solvent extraction).

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

4. Precision and Accuracy

4.1. In a single laboratory (Water Quality Division), the coefficient of variation at a copper level of 10 ug/l was ±1.6% using the solvent extraction method.

IRON

1. Detection Limit

1.1. Direct Aspiration: 0.05 mg/l.

2. Stock Solution

2.1. Stock iron solution, 1000 mg/l Fe: Dissolve 1.000 g pure iron wire in 5 ml conc HNO_3, warming if necessary. Dilute to 1 litre in a volumetric flask.

3. Instrument Parameters

3.1. Lamp: Iron.

3.2. Wavelength: 248.3 mu.

3.3. Slit: 3.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

LEAD

1. Detection Limit

1.1. Direct aspiration: 0.05 mg/l Pb.

1.2. Solvent extraction: 0.001 mg/l Pb.

2. Stock Solution

2.1. Stock lead solution, 1000 mg/l Pb: Dissolve 1.599 g anhydrous lead nitrate, $Pb(NO_3)_2$, in deionized water. Add 10 ml of conc HNO_3 and dilute to 1 litre with deionized water.

3. Instrument Parameters

3.1. Lamp: Lead.

3.2. Wavelength: 283.3 mu.

3.3. Slit: 4.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

4. Precision and Accuracy

4.1. In a single laboratory (Water Quality Division), the coefficient of variation at a lead level of 10 ug/l Pb was ±2.2% using the solvent extraction method.

LITHIUM

1. Detection Limit

1.1. Direct aspiration: 0.005 mg/l Li.

2. Stock Solution

2.1. Stock lithium solution, 100 mg/l Li: Dissolve 0.6109 g anhydrous lithium chloride, LiCl, in deionized water and dilute to 1 litre.

3. Instrument Parameters

3.1. Lamp: Lithium.

3.2. Wavelength: 670.8 mu.

3.3. Slit: 4.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

MAGNESIUM

1. Range and Detection Limit

1.1. Range: 0.01 - 2 mg/l Mg. The upper range can be extended by dilution of the original sample.

1.2. Detection Limit: 0.001 mg/l Mg.

2. Reagents

2.1. Lanthanum chloride solution, 10% La: Weigh 117.2 g lanthanum oxide, La_2O_3, and transfer to a 1-litre beaker. Add about 600 ml deionized water followed by 200 ml conc HCl. Heat the beaker and stir the mixture until the salt has been dissolved. Cool, filter into a one-litre flask and make up to the mark with deionized water. Store in a polyethylene bottle.

2.2. Stock magnesium solution, 500 mg/l Mg: Dissolve 0.829 g magnesium oxide, MgO, in 10 ml conc HNO_3 and dilute to 1 litre with deionized water.

2.3. Standard solutions: Prepare a series of standard solutions from 0.0 to 2 mg/l by dilution of the stock magnesium solution (2.2). To each 1000 ml of working solution prepared add 20.0 ml of 10% lanthanum solution (2.1) to make a total volume of 1020 ml.

2.4. Blank solution: This solution is used to run the base line and is prepared by adding 20.0 ml lanthanum solution (2.1) to 1 litre of deionized water.

3. Procedure

3.1. Pipette a 25-ml sample into a 50-ml Erlenmeyer flask.

3.2. To the sample add 0.5 ml lanthanum solution (2.1) and mix by swirling the flask.

3.3. Establish a base line by aspirating the blank solution (2.4).

3.4. Aspirate standard magnesium solutions and sample, and record readings. Calculate results as outlined in Calculations, 9 (See Metals).

4. Instrument Parameters

4.1. Lamp: Calcium-Magnesium.

4.2. Wavelength: 285.2 mu.

4.3. Slit: 5.

4.4. Burner: 2-inch single slot placed crossways to light path.

4.5. Fuel: Acetylene.

4.6. Oxidant: Air.

4.7. Type of Flame: Reducing.

5. Precision and Accuracy

5.1. In a single laboratory (Water Quality Division), the coefficient of variation at a magnesium level of 2.0 mg/l Mg was ±0.5%.

1. Detection Limit

1.1. Direct aspiration: 0.01 mg/l Mn.

1.2. Solvent extraction: 0.001 mg/l Mn.

2. Reagents

2.1. Stock manganese solution, 1000 mg/l Mn: Dissolve 2.747 g manganese sulphate, $MnSO_4$, previously dried at 180°C for one day, in deionized water in a 1-litre volumetric flask and make up to volume.

2.2. Oxine reagent: Dissolve 1.0 g oxine (8-hydroxy-quinoline) in 100 ml methyl isobutyl ketone (MIBK).

2.3. Ammonia solution: Mix 1 part conc ammonium hydroxide, NH_4OH, with 3 parts of deionized water.

3. Procedure for Low Levels of Manganese (0.001 to 0.020 mg/l Mn).

3.1. Place a 100-ml sample that has been adjusted to a pH 9-11 using ammonia solution (2.3) in a 250-ml volumetric flask.

3.2. Prepare a series of manganese standards from 0.0 to 20 ug/l, adjust pH to 9-11 using ammonia solution and place into 250-ml volumetric flasks. Add deionized water to a total volume of approximately 100 ml.

3.3. To each add 6.0 ml oxine reagent (2.2) and shake the flasks for 5 min.

3.4. Allow the layers to separate and then float the organic layer of each flask to the top by adding deionized water slowly down the sides of the flasks.

3.5. Aspirate standards and sample using oxine reagent (2.2) to establish a base line.

4. Instrument Parameters

4.1. Lamp: Manganese.

4.2. Slit: 4.

4.3. Wavelength: 279.8 mu.

4.4. Burner: Boling.

4.5. Fuel: Acetylene.

4.6. Oxidant: Air.

4.7. Type of Flame: Oxidizing.

5. Precision and Accuracy

5.1. In a single laboratory (Water Quality Division), the coefficient of variation at a manganese level of 10 ug/l Mn was ±4.0% using the solvent extraction method.

MERCURY

(Atomic Absorption Method)

1. Scope and Application

1.1. This atomic absorption method is applicable to surface, ground and saline waters and industrial wastes. Depending upon instrument settings, concentrations in the range between 0.05 and 100 ug/l Hg may be determined. Higher mercury levels can be measured by appropriate dilution of an aliquot.

2. Principle of Method

2.1. The organomercury compounds in the sample are oxidized to inorganic mercury compounds by heating with sulphuric acid and potassium permanganate in an automated system. This automated system provides not only the advantages of speed and reliability but also a closed system where the oxidation can take place at a high temperature with no loss of volatile organomercurys.

2.2. After oxidation, the mercuric compounds are then reduced with stannous sulphate in a hydroxylamine sulphate-sodium chloride solution to elemental mercury. This elemental mercury is sparged from the solution with a stream of air and passed through a cell mounted on the burner in an atomic absorption spectrophotometer. The cell is situated in the light path and the absorption is measured; a mercury hollow cathode lamp is used as the light source.

3. Interferences

3.1. There are no known significant interferences.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a thoroughly cleaned polyethylene bottle. The treatment of the sample at the time of collection will determine the type of data obtained from the analyses, i.e., dissolved, total, etc. Refer to Sample Preparation (5) for explanation of measurements in order that the proper sampling technique will be used for the type of data required.

4.2. If the sample is not acidified at the time of collection, there is a rapid loss of mercury from solution in a matter of hours.

4.3. Limited experience with storage of dilute mercury solutions in glass bottles indicates that even at low pH, there is a rapid loss from solution and it is recommended that glass bottles not be used.

5. Sample Preparation

5.1. Dissolved mercury: Sample should be free from turbidity or filtered through a 0.45-micron membrane filter and acidified (1 ml conc H_2SO_4 per 100-ml sample) immediately. The sample should be filtered at the time of collection.

5.2. Suspended mercury: Sample is filtered through 0.45-micron membrane filter at time of collection, and analysis carried out on the portion of the sample retained on the filter. The sample retained on the filter is prepared for analysis as follows:

5.2.1. Transfer the filter with its contents to a small beaker and cover the filter with conc H_2SO_4. Digest at room temperature for several hours and then make up with distilled water to the original volume of sample that was filtered.

5.3. Total mercury: Sum of the concentrations is the dissolved and suspended fractions.

5.4. Extractable mercury: Dissolved concentration plus the concentration of mercury from the suspended solids (turbidity) that is dissolved by acidification with conc H_2SO_4 (1 ml per 100-ml sample). In many cases, this represents the total mercury content if all sediment was dissolved.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler II.

6.1.2. Manifold.

6.1.3. Heating bath (105°C) containing two mixing coils (#116-0163). A beaker containing mineral oil and placed on a stirring hot-plate is suitable as a heating bath. Stir with a teflon stirring bar.

6.2. Atomic Absorption Spectrophotometer, Perkin Elmer Model 403, or equivalent.

6.3. Recorder, Perkin Elmer Model 165, or equivalent.

6.4. Proportioning Pump, Carlo Erba No. 08-59-10202 (available from Allied Scientific Company Ltd., 317 Progress Ave., Scarborough, Ontario).

6.5. Gas separator; construct as shown in Figure 6.

6.6. Absorption cell, made from borosilicate glass tubing, 10-mm I.D., 100-mm long. The ends are ground square and quartz windows are attached with epoxy cement. Gas inlet and outlet parts are attached approximately 5 mm from each end of the cell. Gas connections are made with 0.0625-inch I.D., 0.130-inch O.D. Technicon transmission tubing. The absorption cell is placed in a wooden frame mounted on top of one of the burners and fixed in position with masking tape.

6.7. Lamp, 60-Watt bulb, arranged to shine on the absorption cell to prevent condensation of moisture inside the cell.

7. Reagents

7.1. Hydroxylamine sulphate-sodium chloride solution: Dissolve 15 g hydroxylamine sulphate, $(NH_2OH)_2.H_2SO_4$, and 15 g sodium chloride, NaCl, in 500 ml distilled water. Prepare daily.

7.2. Potassium permanganate solution: Dissolve 2.5 g potassium permanganate, $KMnO_4$, in 500 ml distilled water. Prepare weekly.

7.3. Stannous sulphate solution: Dissolve 25 g stannous sulphate, $SnSO_4$, in 250 ml 2N sulphuric acid. Prepare daily.

7.4. Sulphuric acid, H_2SO_4, concentrated.

7.5. Stock mercury solution, 100 mg/l Hg: Dissolve 0.0168 g phenyl mercuric acetate in 1N sulphuric acid in a 100-ml volumetric flask and make up to the mark with 1N sulphuric acid.

7.6. Working mercury solutions: Dilute stock mercury solution (7.5) to prepare appropriate working standards.

8. Procedure

8.1. Run the standards and samples using the manifold shown in Figure 5 and the instrument settings shown in Table 1.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of mercury in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at mercury concentrations of 0.3, 2.0 and 8.0 ug/l were ±5.5, ±4.9, and ±3.3% respectively.

11. Reference

11.1. Goulden, P.D. and B.K. Afghan, 1970. An Automated Method for Determining Mercury in Water. Inland Waters Branch, Department of Energy, Mines and Resources. Technical Bulletin No. 27.

TABLE 1

Instrument Settings (Perkin-Elmer Model 403) for Different Levels of Mercury

MERCURY LEVEL ug/l	SAMPLES PER HOUR	RECORDER FULL SCALE	CONCENTRATION DIAL
0.05 - 0.5	20	1A	500
0.5 - 10	20	2A	500
10 - 100	20	4A	100

ALL LEVELS	MODE - "CONCENTRATION"	-	"10 AVERAGE"
	RECORDER RESPONSE	-	3
	CHART SPEED	-	5 mm/min
	SLIT SETTING	-	6
	WAVELENGTH	-	253.7 mu

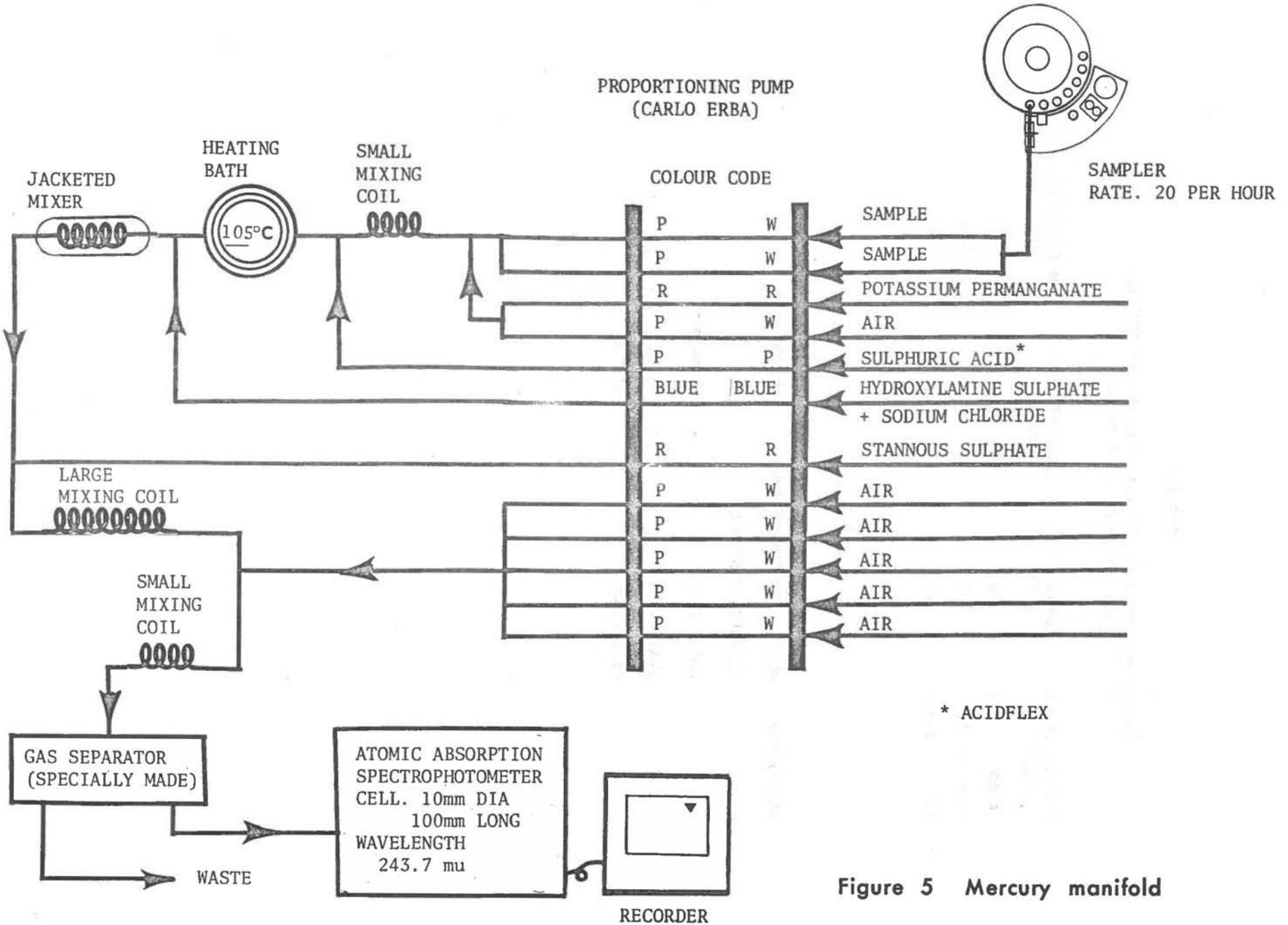

Figure 5 Mercury manifold

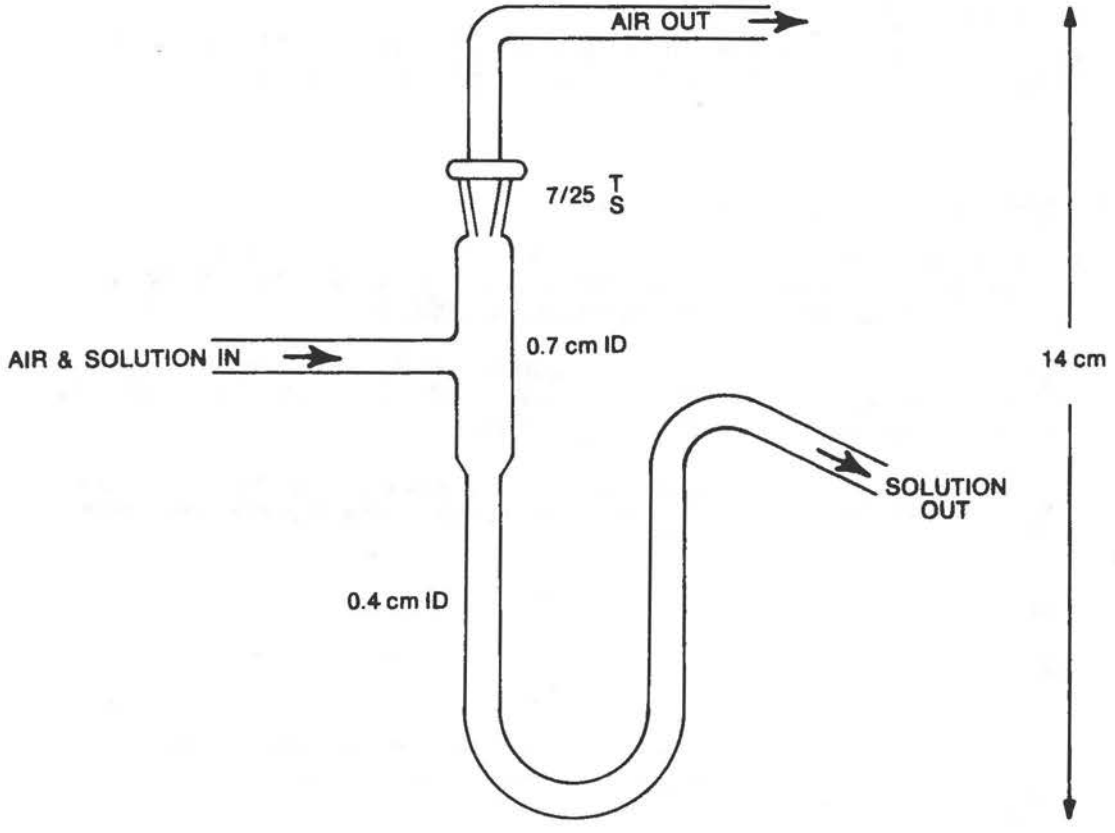

Figure 6 Gas separator

MOLYBDENUM

1. Detection Limit

1.1. Direct aspiration: 0.05 mg/l.

1.2. Solvent extraction: 0.2 ug/l.

2. Reagents for Low Level Determination

2.1. Complexing agent: Dissolve 10 g benzoin α-oxime in 1 litre ethyl alcohol.

2.2. Solvent: n-butylacetate.

2.3. Bromine water: 1% solution.

2.4. Stock molybdenum solution, 1000 mg/l Mo: Dissolve 1.840 g ammonium molybdate, $(NH_4)_6\ MO_7O_{24}.4H_2O$, in deionized water and make up to 1 litre.

3. Procedure for Low Level Determination

3.1. Place 150-ml sample that has been adjusted to a pH 1.6, (this will be the pH of most samples if they were preserved using 2 ml conc HNO_3 per litre of sample) in a 200-ml volumetric flask.

3.2. Prepare a series of molybdenum standards from 0.0 to 10 ug/l, adjust pH to 1.6 and place into 200-ml volumetric flasks. Add deionized water to a total volume of approximately 150 ml.

3.3. To each flask add 0.5 ml bromine water and warm on a water bath until nearly all the colour due to the bromine water has disappeared; then cool to room temperature.

3.4. Add 5.0 ml complexing agent to each flask and mix.

3.5. Add 3.0 ml n-butylacetate to each and shake the flasks for 5 min on a mechanical shaker.

3.6. Allow the layers to separate and float the organic layer of each flask to the top by slowly adding deionized water down the side of the flask.

3.7. Aspirate the organic layer of each standard and sample and record readings.

4. Instrument Parameters

4.1. Lamp: Molybdenum.

4.2. Wavelength: 313.5 mu.

4.3. Slit: 4.

4.4. Burner: Nitrous oxide.

4.5. Fuel: Acetylene.

4.6. Oxidant: Nitrous oxide.

4.7. Type of Flame: Reducing.

NICKEL

1. Detection Limit

1.1. Direct aspiration: 0.01 mg/l Ni.

1.2. Solvent extraction: 0.001 mg/l Ni.

2. Stock Solution

2.1. Stock nickel, 100 mg/l Ni: Dissolve 0.4479 g nickel sulphate, $NiSO_4.6H_2O$, in distilled water and dilute to 1 litre in a volumetric flask.

3. Instrument Parameters

3.1. Lamp: Nickel.

3.2. Wavelength: 232.0 mu.

3.3. Slit: 3.

3.4. Burner: Boling.

3.5. Fuel: Acetylene.

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

4. Precision and Accuracy

4.1. In a single laboratory (Water Quality Division), the coefficient of variation at a nickel level of 10 ug/l Ni was ±3.8% using the solvent extraction method.

SILVER

1. Detection Limit

1.1. Direct aspiration, 0.01 mg/l Ag.

1.2. Solvent extraction, 0.005 mg/l Ag.

2. Sampling Procedure and Storage

2.1. Dry disodium salt of EDTA at a rate of 0.4 g for each 100-ml sample should be added to the sample container before collection. The sample bottle should not be rinsed with the sample before filling the bottle. The sample should be analyzed within 10 days of sampling.

3. Reagents

3.1. Silver stock solution, 100 mg/l Ag: Dissolve 0.0787 g silver nitrate, $AgNO_3$, in distilled water and dilute to 500 ml in a volumetric flask. This stock solution must be prepared fresh each day.

3.2. Dithizone solution: Dissolve 0.05 g diphenylthiocarbazone in 100 ml ethyl propionate. This solution should be prepared every three weeks.

3.3. Acetone.

3.4. EDTA, 0.01 M,: Dissolve 3.72 g disodium salt of EDTA in distilled water and dilute to 1 litre.

4. Procedure

4.1. Determination of silver in the range 0.005 to 0.050 mg/l.

4.1.1. Pipette a 100-ml sample into a 250-ml separatory funnel. The pH of the sample should be between 3.5 and 6.5. If EDTA was used as a preservative, the pH (for most waters) will be between 4.0 and 5.0.

4.1.2. Add 10.0 ml dithizone-ethyl propionate solution (3.2) and shake the separatory funnel for 1 min using short rapid strokes.

4.1.3. Allow about 10 min for the separation of the aqueous and solvent phases; then drain the aqueous phase to waste.

4.1.4. Wipe the stem of the separatory funnel dry, as the presence of moisture is critical.

4.1.5. Drain the solvent into a dry test tube provided with a tight inert stopper.

4.1.6. Add 1.0 ml acetone to the sample extract in the test tube to eliminate problems caused by any remaining minute droplets of water entrapped in the solvent.

4.1.7. Treat standard solutions in the same manner after adding suitable aliquots of the standard silver solution to separatory funnels and diluting to volume with 0.01 M EDTA.

4.1.8. Aspirate sample and standards using a dithizone-ethyl propionate solution for establishing a base line.

4.2. For higher concentrations of silver use the direct aspiration procedure.

5. Instrument Parameters

5.1. Lamp: Silver.

5.2. Wavelength: 328.1 mu.

5.3. Slit: 4.

5.4. Burner: 4-inch single slot.

5.5. Fuel: Acetylene.

5.6. Oxidant: Air.

5.7. Type of Flame: Oxidizing.

STRONTIUM

1. Detection Limit

1.1. Direct aspiration: 0.02 mg/l.

2. Principle of Method

2.1. By adding known quantities of standard strontium solutions (standard addition) to the sample aliquot, then measuring the absorbance, the strontium concentration of the sample can be found.

3. Stock Solution

3.1. Stock strontium solution, 1000 mg/l Sr: Into a 500-ml Erlenmeyer flask add 1.685 g anhydrous strontium carbonate, $SrCO_3$, powder. Place a funnel in the neck of the flask and add 1 + 1 HCl, a little at a time, until all the $SrCO_3$ has dissolved. Add 200 ml distilled water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange colour by adding 3N NH_4OH or 1 + 1 HCl as required. Transfer quantitatively to a 1-litre volumetric flask and dilute to the mark with distilled water.

4. Instrument Parameters

4.1. Lamp: Strontium.

4.2. Wavelength: 460.7 mu.

4.3. Slit: 4.

4.4. Burner: Boling.

4.5. Fuel: Acetylene.

4.6. Oxidant: Air.

4.7. Type of Flame: Reducing.

5. Procedure

5.1. Make an approximate estimate of the strontium concentration in the water sample in order to determine the amount of strontium standard solution to be added.

5.2. Pipette three 20-ml aliquots of the sample into three Erlenmeyer flasks. To one flask add 5 ml deionized water. To the other two add 5 ml suitable standard solution, e.g., for a concentration of approximately 0.5 mg/l Sr ion, a final concentration of about 1.0 mg/l Sr is required.

5.3. Aspirate samples and record readings.

6. Calculations

6.1. The Strontium ion concentration in solution is proportional to the absorbance at the atomic resonance wavelength.

i.e., $x = KA...$

where x is the Sr sample concentration, K is the proportionality constant and A is the instrument reading. On adding the suitable standard of concentration "a", the new instrument reading is A' but K remains the same. Hence, $(x + a) = KA'$ and x can be found by elimination.

7. Precision and Accuracy

7.1. In a single laboratory (Water Quality Division), the coefficient of variation at a concentration of 200 ug/l Sr was ±1.0%.

VANADIUM

1. Detection Limit

1.1. Direct aspiration: 0.05 mg/1.

1.2. Solvent extraction: 0.5 ug/1.

2. Reagents for Low Level Determination

2.1. Complexing agent: Dissolve 10 g cupferron in 1 litre deionized water.

2.2. n-Butylacetate.

2.3. Bromine water: 1% solution.

2.4. Stock vanadium solution, 1000 mg/1 V: Dissolve 1.785 g pure vanadium pentoxide, V_2O_5, previously ignited at 500°C, in a slight excess of sodium hydroxide, then add a slight excess of sulphuric acid and dilute to 1 litre.

3. Procedure for Low Level Determination

3.1. Place a 150-ml sample that has been adjusted to a pH 1.6 (this will be the pH of most samples if they were preserved using 2 ml conc HNO_3 per litre of sample) in a 200-ml volumetric flask.

3.2. Prepare a series of vanadium standards from 0.0 to 20 ug/1, adjust pH to 1.6 and place into 200-ml volumetric flasks. Add deionized water to a total volume of approximately 150 ml.

3.3. To each flask add 0.5 ml bromine water and warm on a water bath until all the colour due to the bromine water has disappeared; then cool to room temperature.

3.4. Add 5.0 ml complexing agent to each flask and mix.

3.5. Add 3.0 ml n-butylacetate to each and shake the flasks on a mechanical shaker for 5 min.

3.6. Allow the layers to separate and float the organic layer of each flask to the top by slowly adding deionized water down the side of the flask.

3.7 Aspirate the organic layer and record readings.

4. Instrument Parameters

4.1. Lamp: Vanadium.

4.2. Wavelength: 318.4 mu.

4.3. Slit: 4.

4.4. Burner: Nitrous oxide.

4.5. Fuel: Acetylene.

4.6. Oxidant: Nitrous oxide.

1. Detection Limit

1.1. Direct aspiration: 0.01 mg/l Zn.

1.2. Solvent extraction: 0.001 mg/l Zn.

2. Stock Solution

2.1. Stock zinc solution, 1000 mg/l Zn: Dissolve 1.000 g zinc metal, Zn, in 10 ml conc HNO_3. Dilute to 1 litre with deionized water.

3. Instrument Parameters

3.1. Lamp: Zinc.

3.2. Wavelength: 213.8 mu.

3.3. Slit: 5.

3.4. Burner: 1. Low temperature (direct aspiration).
2. 4-inch single slot (solvent extration).

3.5. Fuel: 1. Propane (direct aspiration).
2. Acetylene (solvent extraction).

3.6. Oxidant: Air.

3.7. Type of Flame: Oxidizing.

4. Precision and Accuracy

4.1. In a single laboratory (Water Quality Division), the coefficient of variation at a zinc level of 10 ug/l Zn was ±1.4% using the solvent extraction method.

NITRILOTRIACETIC ACID (NTA)

(Polarographic Method)

1. Scope and Application

1.1. This differential polarographic method is applicable to the determination of nitrilotriacetic acid (NTA) in natural waters in the range 0.025 to 1.0 mg/litre. Higher concentrations can be determined by slight modifications to the method. The method can also be used to determine NTA in detergents.

1.2. The detection limit of the method is 10 ug/l NTA.

2. Principle of Method

2.1. This method for the determination of nitrilotriacetic acid in natural waters and detergents is based on the formation of bismuth - NTA complex at pH 2.0 ±0.05. The resultant complex is analysed using a differential cathode ray polarograph. This technique utilizes a two-cell operation and eliminates all cell currents not of interest in the analysis. The twin cell circuitory enables a resultant signal from the reference cell, containing all reagents, to be balanced with the sample solution. Therefore, full use of current sensitivity of the instrument is made to measure very small quantities of NTA.

3. Interferences

3.1. The method has been tested in the presence of metal ions which form complexes with NTA, closely related aminopolycarboxylic acids, amino acids, pyro -, hexameta - and tripoly phosphate. There are no known significant interferences from above compounds except large excess of iron (111), which gives a prewave close to bismuth-NTA wave. Addition of hydroxylamine hydrochloride or ascorbic acid eliminates this interference by reducing iron (111) to iron (11).

4. Sampling Procedure and Storage

4.1. The water sample should be collected in a thoroughly cleaned polyethylene bottle, filtered through a 0.45-micron membrane filter and acidified to pH 1.0 with hydrochloric acid. Acidification of sample prevents the further biodegradation of NTA in the sample. This procedure is only applicable to concentrations of NTA below 250 ug/litre. At higher concentrations, acidification of the sample might result in precipitation of NTA. Therefore, at higher concentrations, the sample should be preserved at 4°C without acidification.

5. Sample Preparation

5.1. The sample used for analysis should be as free from turbidity as possible. Slight traces of turbidity should be removed by filtering the sample through a 0.45-micron membrane filter before analysis.

6. Apparatus

6.1. Davis Differential Cathode Ray Polarograph type A-1660, manufactured by Southern Analytical Limited, Surrey, England.

6.2. Capillaries supplied by Southern Analytical Limited. Mark a capillary tube with a glass knife or ampoule file exactly in the centre and divide into two. Use the newly cut faces as the working orifices Match the capillaries used in two cells so that when the mercury drop rates are adjusted (11 ±0.2 seconds) the signals from the two cells with the same solutions in them are effectively identical.

7. Reagents

7.1. Hydroxylamine hydrochloride solution, 1%: Dissolve 1 g hydroxylamine hydrochloride, $NH_2OH.HCl$, in 100 ml deionized water.

7.2. Bismuth stock solution, 10^{-3}M: Dissolve 0.4851 g bismuth nitrate pentahydrate, $Bi(NO_3)_3.5H_2O$, in 166.7 ml of 6N hydrochloric acid solution and dilute to 1 litre with deionized water.

7.3. Potassium hydroxide solution, 0.5N: Dissolve 28 g potassium hydroxide, KOH, in 1 litre deionized water.

7.4. Hydrochloric acid, 1N: Dilute 77 ml conc hydrochloric acid, HCl, to 1 litre with deionized water.

7.5. Stock NTA solution, 100 mg/l NTA: Dissolve 0.1 g NTA in 10 ml 0.1N sodium hydroxide solution and dilute to 1 litre.

7.6. Standard NTA solution, 10 mg/l NTA: Dilute 10 ml stock NTA solution (7.5) to 100 ml with deionized water.

8. Procedure

8.1. Preparation of calibration curve.

8.1.1. Transfer 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0-ml aliquots standard NTA solution (7.6) to 50-ml beakers.

8.1.2. Add 4.5 ml 1N hydrochloric acid solution to all beakers except blank; add 5.0 ml 1N hydrochloric acid to the blank.

8.1.3. Add 1.0 ml hydroxylamine hydrochloride solution to all beakers.

8.1.4. Add 0.5 ml bismuth solution to all beakers except blank.

8.1.5. Add 25 ml deionized water to all beakers.

8.1.6. Adjust pH of the solution to 2.0 ±0.05 with KOH solution (7.3).

8.1.7. Transfer the content of beaker to 50-ml volumetric flask and dilute to mark with deionized water.

8.1.8. Add 1 ml triple-distilled mercury to the two cells.

8.1.9. Transfer 5 ml of blank containing no bismuth to cell 2 and an equivalent amount of the lowest standard to cell 1.

8.1.10. Bubble nitrogen through the solutions at an equal rate for 10 minutes.

8.1.11. Lower the capillaries into the cells, ensuring that the skirt forms a water seal and degas for a further five minutes. Turn off the gas flow.

8.1.12. Polarograph the solution between 0.0 and -0.5V vs mercury pool reference electrode. The applied potential affects the surface tension of the mercury and hence alters the area of electrode. Therefore, for quantitative work, it is essential that the start potential be kept the same (from 0.0 to -0.5V) for samples and their corresponding standard solution.

8.1.13. Repeat for all standard solutions starting at 8.1.8.

8.2. Analysis of water sample

8.2.1. Transfer two, 25-ml sample aliquots into separate beakers (one is test sample, the other is the blank).

8.2.2. Add 4.5 ml of 1N hydrochloric acid solution to all beakers except the blank; add 5.0 ml of 1N hydrochloric acid solution to the blank.

Note - It is necessary to maintain a concentration of 0.1N HCl in the final 50-ml volume. Therefore, if the sample was preserved with HCl to a pH of 1.0 add 2.5 ml 1N HCl to the blank and 2.0 ml to the test sample.

8.2.3. Proceed as for the preparation of calibration curve starting at 8.1.3.

During analysis of sample, the natural drop rate of capillaries should be identical to the drop rate of electrodes during the preparation of the calibration curve as the peak height is altered when drop rate changes. This is normally done by cleaning the tips of capillaries with 1:1 nitric acid or adjusting the height of the mercury reservoirs or changing the capillaries of dropping mercury electrodes.

8.2.4. If concentration of NTA in sample is too high for the calibration curve, a smaller sample aliquot may be used. It is also possible to use stronger solutions of bismuth and prepare calibration curves for higher ranges.

8.3. To determine NTA in a sample of detergent, dissolve 0.25 g of the detergent in 1 litre deionized water and carry out the analysis as detailed above for a water sample.

9. Calculations

9.1. Measure the peak height at the peak potential due to bismuth-NTA (-0.32V) complex using suitable shunt scale and amplification scale settings. Convert the observed peak height to the peak height at maximum sensitivity by multiplying the observed peak height by the sensitivity and by the amplification factor (settings on instrument).

9.2. Repeat the above procedure for all the points in calibration curve.

9.3. Prepare calibration curve by plotting peak height at maximum sensitivity vs concentration of NTA.

9.4. Determine concentration of NTA in the sample by comparing sample peak height at maximum sensitivity with calibration curve and correcting for volume of sample used for test, i.e., multiplying value obtained from calibration curve by $\frac{50}{X}$, where X = ml sample.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at 50 and 100 ug/litre NTA were ±3.8 and ±8.9 respectively.

11. Reference

11.1. Afghan, B.K. and P.D. Goulden. Determination of trace quantities of nitrilotriacetic acid by differential cathode ray polarograph. Submitted to Environmental Science and Technology Journal for publication at the time of publication of this manual.

NITROGEN, AMMONIA

(Automated O-Tolidine Method)

1. Scope and Application

1.1 This automated method is applicable to the determination of ammonia in surface waters in the range 1 to 150 ug/l. Higher concentrations can be determined by appropriate dilution of an aliquot or by slight modification of the method.

2. Principle of Method

2.1. Ammonia in a sample is chlorinated in the presence of borate buffer, excess hypochlorite is destroyed and the chlorinated ammonia is determined with O-tolidine.

3. Interferences

3.1. There are no significant interferences. Ions that normally would interfere are removed by dialysis.

4. Sampling Procedure and Storage

4.1. The sample container should be tightly capped immediately after collection of the sample and analysis carried out the same day.

5. Sample Preparation

5.1. The sample used for analyses should be obtained by decantation of the sample container. The sample used for analyses should be as free as possible from turbidity. Slight traces of turbidity will be removed by dialysis.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler.

6.1.2. Manifold.

6.1.3. Proportioning pump.

6.1.4. Dialyzer.

6.1.5. Heating bath (40°C).

6.1.6. Colourimeter equipped with a 50-mm flow cell and 420-mu filters.

6.1.7. Range expander.

6.1.8. Recorder.

7. Reagents

7.1. Alkaline complexing agent:

7.1.1. Dissolve 52 g sodium hydroxide, NaOH, in 1 litre deionized water.

7.1.2. Dissolve 40 g sodium hexametaphosphate in 1 litre deionized water.

7.1.3. Mix 100 ml of each of the above solutions daily.

7.2. Buffer: Dissolve 96 g disodium hydrogen phosphate hydrated, and 10 g sodium dihydrogen phosphate in 5 litres deionized water. (pH 7.5)

7.3. Sodium hypochlorite: Dilute sodium hypochlorite solution (Javex is suitable) to approx. 0.004% available chlorine with deionized water.

7.4. Oxalic acid: Dissolve 20 g oxalic acid and 170 g monochloracetic acid in deionized water and make up to 1 litre.

7.5. Ortho-tolidine: Prepare by heating 1.2 g O-tolidine dihydrochloride in 120 ml conc hydrochloric acid, HCl, at 60°C for 1 hr; then adjust to a volume of 1 litre with distilled water.

7.6. Stock ammonia solution: Dissolve 3.819 g anhydrous ammonium chloride, NH_4Cl, dried at 100°C, in distilled water and dilute to 1 litre. This solution contains 1000 mg/l N.

7.7. Intermediate ammonia solution 10 mg/l: Dilute 10.00 ml stock ammonia solution (7.6) to 1 litre with deionized water.

7.8. Standard ammonia solution, 1 mg/l N: Dilute 100 ml intermediate ammonia solution (7.7) to 1 litre with deionized water.

7.9. Working ammonia standards: Using standard ammonia solution (7.8) prepare working ammonia standards in 100-ml volumetric flasks. Prepare fresh each week. The following standards are suggested:

Ammonia - N, mg/l	ml Standard Solution / 100 ml
0.002	0.2
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
0.15	15.0
0.20	20.0

8. Procedure

8.1. The sample tray (sampler 11) is filled with samples and standards and covered with saran wrap to prevent contamination from the atmosphere.

8.2. The probe used with the sampler is a metallic needle-type that pricks the saran wrap to withdraw samples.

8.3. Samples and standards are run at a rate of 20/hr using the manifold shown in Figure 7.

8.4. Samples high in ammonia may be determined by any one or a combination of two or more of the following:

8.4.1. Replace colourimeter (50 mm) with a colourimeter equipped with a 15 or 8-mm flow cell.

8.4.2. Remove range expander.

8.4.3. Replace sample line with a smaller line and add a distilled water line to make up the volume difference.

8.4.4. Dilution of the sample prior to loading on the sample tray.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of ammonia in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at ammonia levels of 10 and 50 ug/l N were ±4.53% and ±1.69% respectively.

11. Reference

11.1. Sawyer, R. and L.M. Grisley. The determination of Ammonia in the ppb Level in Solution. Technicon Symposia, 1967, vol. 1. Automation in analytical chemistry.

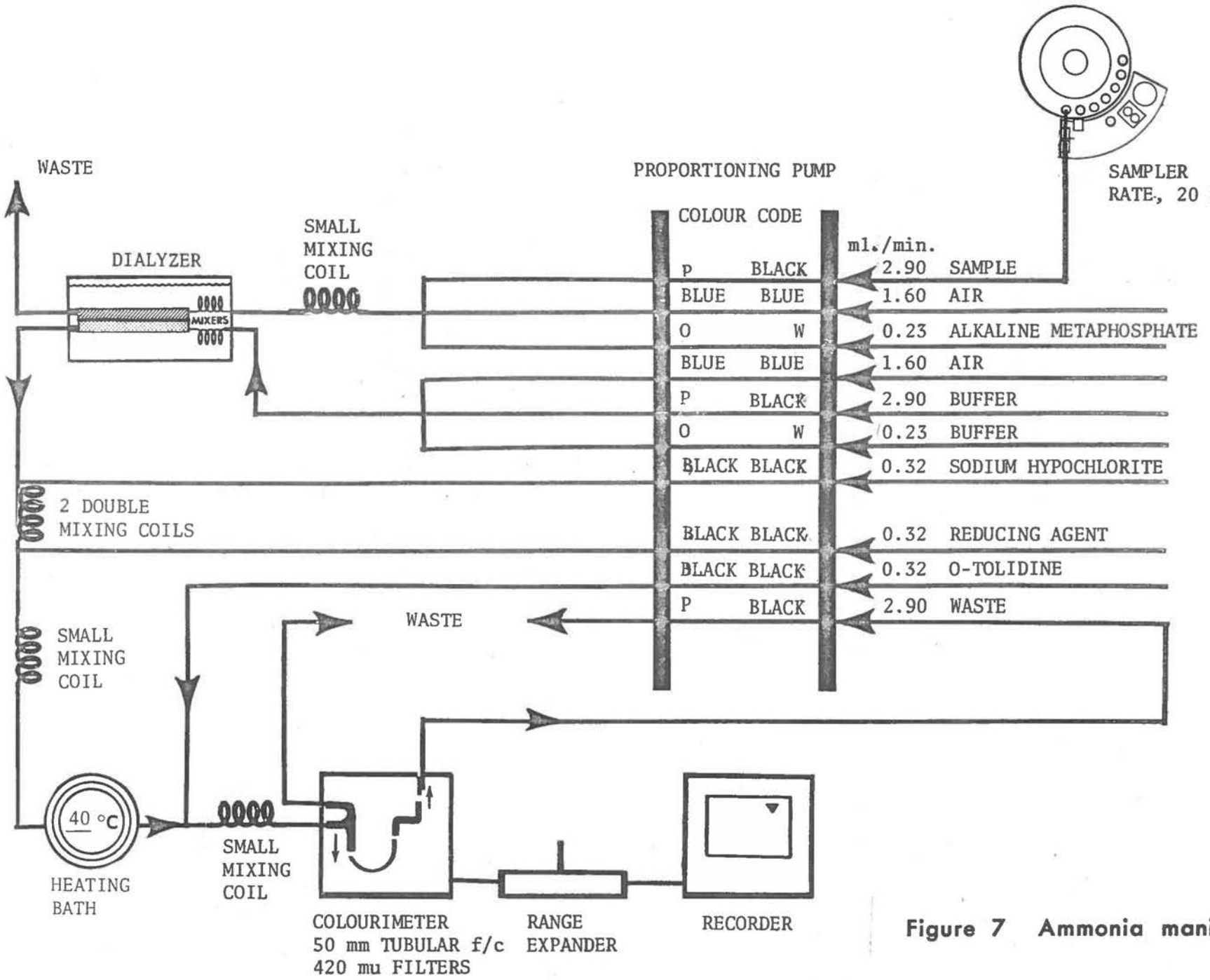

Figure 7 Ammonia manifold

NITROGEN, NITRATE - NITRITE

(Automated Cadmium Reduction Method)

1. Scope and Application

1.1. This method is applicable to the determination of nitrate and nitrite, singly or combined, in surface, ground and waste waters in the range 0.1 to 5.0 mg/l N. The method is extremely sensitive and as little as 0.001 mg/l N can be determined with slight modification.

2. Principle of Method

2.1. The sample is passed through a coil containing cadmium filings that reduce the nitrates present to nitrites. The resulting nitrites plus those originally present are then reacted with sulphanilamide to form the diazo compound. The coupling reaction is carried out on the diazotized sample by the addition of naphthylethylene diamine dihydrochloride to form the azo dye. The azo dye intensity, which is proportional to the nitrate concentration, is then measured.

2.2. Separate nitrite values can be obtained by carrying out the procedure without the cadmium reduction step.

3. Interferences

3.1. There are no significant interferences.

4. Sampling Procedure and Storage

4.1. Analyses should be carried out as soon as possible after collection of the sample, preferably the same day.

5. Sample Preparation

5.1. The sample aliquot used for the analysis either should be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of the following components:

6.1.1. Sampler II.

6.1.2. Manifold (See Figure 8).

6.1.3. Colourimeter equipped with a 50-mm flow cell (or a 15-mm cell for high range) and 550-mu filters.

6.1.4. Range expander.

6.1.5. Recorder.

7. Reagent

7.1. EDTA Reagent (2-2.5% w/v): Dissolve 10.5 g disodium salt of ethylenediamine tetraacetic acid in 450 ml distilled water. Adjust pH to 6.5-7.0 with dilute NaOH. Bring to final volume of 500 ml with distilled water.

7.2. Sulphanilamide reagent: Dissolve 1.0 g sulphanilamide in a mixture of 90 ml distilled water and 10 ml conc hydrochloric acid.

7.3. Naphthylethylenediamine reagent: Prepare a 0.1% w/v solution of N-1 naphthylethylenediamine dihydrochloride and store in an amber glass bottle. This reagent is stable for a few weeks, then it should be discarded.

7.4. Cadmium reduction column: A short mixing coil is packed with cadmium filings (mesh 20). Metal filings can be obtained by using an open type rasp on cadmium metal sticks.

7.5. Stock nitrate solution, 1000 mg/l NO_3 as N: Dissolve 7.218 g potassium nitrate, KNO_3, in distilled water and dilute to 1 litre.

7.6. Stock nitrite solution, 1000 mg/l NO_2 as N: Dissolve 6.072 g potassium nitrite, KNO_2, in distilled water and dilute to 1 litre. This solution is unstable and should be prepared as required.

7.7. Standard nitrate solution, 10 mg/l NO_3 as N: Dilute 10.0 ml stock nitrate solution to 1 litre with distilled water.

7.8. Standard nitrite solution, 10 mg/l NO_2 as N: Dilute 10.0 ml stock nitrite solution to 1 litre with distilled water.

7.9. Working nitrate and nitrite solution: Using the standard nitrate or nitrite solutions (see 7.7 and 7.8) prepare working standards in 100-ml volumetric flasks as follows:

Concentration, mg NO_3-N or NO_2-N/l	Volume of Standard (10 mg/l) diluted to 100 ml
0.00	0.0
0.02	0.2
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.0	10.0
2.0	20.0
4.0	40.0
5.0	50.0

8. Procedure

8.1. Procedure for high range, 0.01 to 5 mg/l N.

8.1.1. Run the samples and standards at 20 per hour using the manifold as shown in Figure 8.

8.2. Procedure for low range, 0.001 to 0.20 mg/l N.

8.2.1. Run the samples and standards as shown in Figure 8 except replace the 15-mm colourimeter with a 50 mm and install a range expander for use at 4X or 10X.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of nitrate + nitrite in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the co-efficient of variation at a concentration of 50 ug/l NO_3 -N was ±1.6%.

11. Reference

11.1. Brewer, P.G. and J.P. Riley. 1965. The Automatic Determination of Nitrate in Sea Water. Deep Sea Research 1965, vol. 12, pp. 765-772.

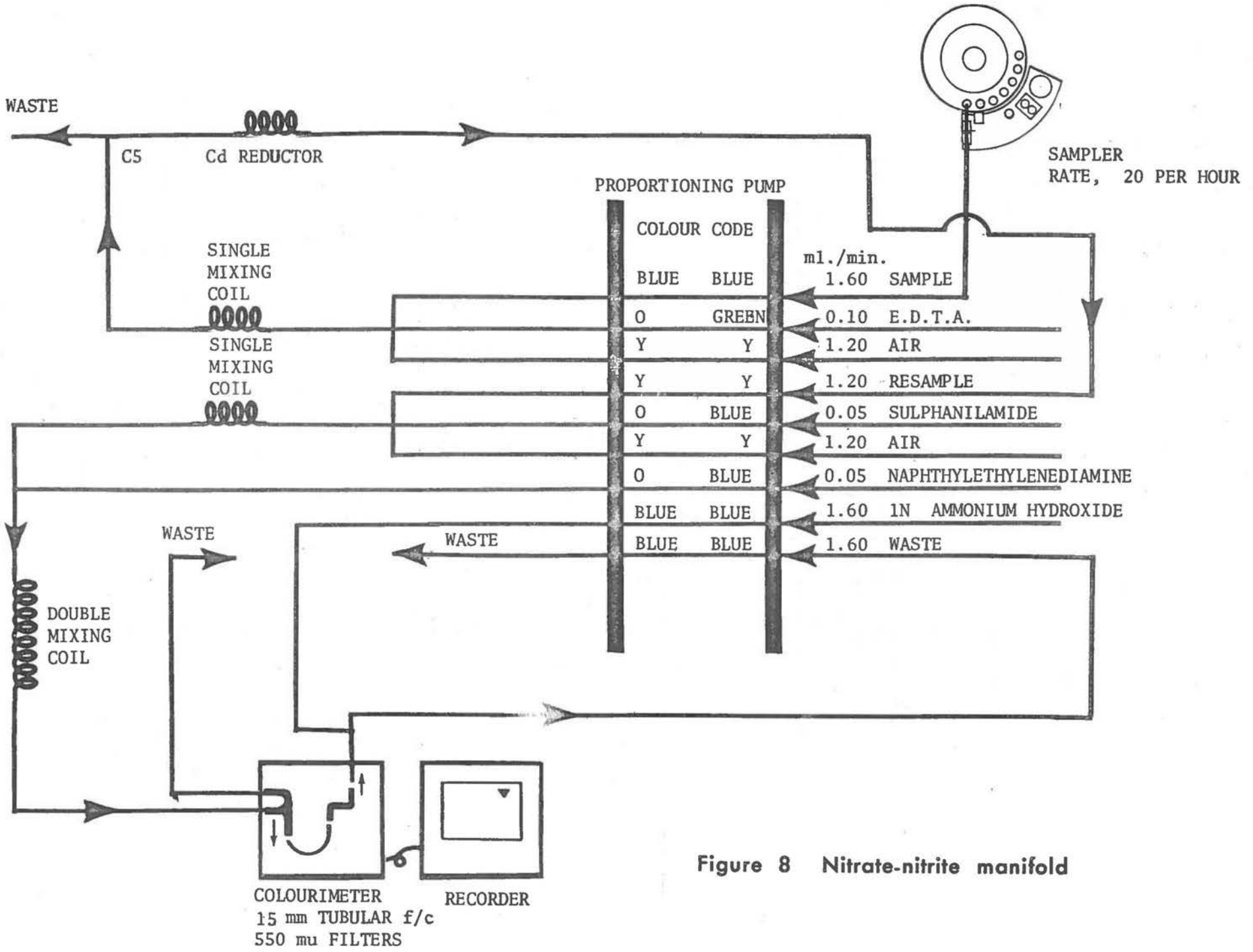

Figure 8 Nitrate-nitrite manifold

NITROGEN, ORGANIC

(Automated Ultra-Violet Digestion Method)

1. Scope and Application

1.1. This method pertains to the determination of organic nitrogen in unpolluted or slightly polluted natural waters. The applicable range is 25 to 1000 ug/l organic nitrogen - N.

2. Principle of Method

2.1. In this automated procedure, organic nitrogen compounds, including ammonia in a sample, are oxidized by ultra-violet irradiation to a mixture of nitrate and nitrite with the measurement of the resultant mixture. Differentiation of different forms of nitrogen is accomplished by determining independently, the nitrate and nitrite and ammonia content without irradiation; organic nitrogen is then determined by subtracting these values obtained from the nitrate and nitrite value obtained on the same sample after irradiation.

3. Interferences

3.1. There are no significant interferences found in normal waters.

3.2. Because the concentration of organic nitrogen is calculated by subtracting the concentrations of ammonia, and nitrate and nitrite from the total nitrogen content, large concentrations of inorganic nitrogen (ammonia, nitrate or nitrite) originally present in a sample will make it difficult to measure low concentrations of organic nitrogen.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a polyethylene bottle and analysed as soon as possible. If the analysis cannot be carried out soon after collection (within 2 days) it should be frozen for storage.

5. Sample Preparation

5.1. If the sample is relatively free from turbidity, such as a sample taken in open waters of any of the Great Lakes, a shaken sample should be placed in the sample cup for analysis and the result called total organic nitrogen.

5.2. If the sample contains large quantities of suspended solids it should be filtered through a 0.45-micron filter and the result, after analysis, called soluble organic nitrogen. To obtain a total organic nitrogen value on such a sample, the method outlined elsewhere in this manual for Total Organic Nitrogen should be followed.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler II.

6.1.2. Two proportioning pumps.

6.1.3. Three colourimeters, two 15-mm flow cells and one 50-mm flow cell and two sets of 550- and one set of 420-mu filters.

6.1.4. Recorders, one two-pen and one single-pen.

6.1.5. Three manifolds, for ammonia (1) and nitrate and nitrite (2).

6.1.6. Dialyzer.

6.1.7. Heating bath, 40°C.

6.2. UV-Reactor

6.2.1. The UV-reactor is constructed using a sheet metal box 13"x12"x15" to house components. A 550-watt photo-chemical lamp is placed inside a fused quartz lamp protection jacket and mounted axially in the centre of the box. Two quartz coils are placed on top of each other so that the same lamp can be used to irradiate both coils. Irradiating coils in the UV-reactor are cooled by a high-speed fan fitted on the side of the reactor box; an exhaust is fitted on the top of the reactor. The quartz coils are made of Purcil 453 quality fused silica tubing of 3 mm-I.D., 0.6-mm wall thickness and with a coil diameter of approximately 5 inches. Prior to entering the manifold, the sample is segmented by purified air which is passed through a scrubber containing 10% sulphuric acid.

7. Reagents

7.1. Reagents for total nitrogen, and nitrate plus nitrite:

7.1.1. Hydrochloric acid solution: Dilute 38.5 ml concentrated hydrochloric acid to five litres with distilled deionized water.

7.1.2. Sodium hydroxide solution: Dissolve 34.0 g sodium hydroxide, 29.8 g disodium hydrogen phosphate and 5.6 g potassium dihydrogen phosphate in distilled deionized water and dilute to five litres.

7.1.3. EDTA Solution: Dissolve 50.0 g disodium salt of ethylenediamine tetraacetic acid in 700 ml distilled deionized water and adjust the pH of the solution to 6.5-7.0 with dilute sodium hydroxide and dilute to 1 litre.

7.1.4. Sulphanilamide solution: Dissolve 5.0 g sulphanilamide in distilled deionized water, add 50 ml conc hydrochloric acid and dilute to 1 litre with distilled deionized water.

7.1.5. Naphthylethylenediamine solution: Dissolve 0.5 g naphthylethylenediamine dihydrochloride in distilled deionized water and dilute to 1 litre.

7.1.6. Stock nitrate solution, 1000 mg/l NO_3 as N: Dissolve 7.218 g potassium nitrate, KNO_3, in distilled deionized water and dilute to 1 litre.

7.1.7. Intermediate nitrate solution, 10 mg/l NO_3 as N: Dilute 10 ml stock nitrate solution (7.1.6) to 1 litre with distilled deionized water.

7.1.8. Standard nitrate solutions: From the intermediate nitrate solution (7.1.7), prepare standard solutions of nitrate to cover the expected range of the samples.

7.2. Reagents for Ammonia

7.2.1. Alkaline hexametaphosphate solution: Dissolve 40.0 g sodium hexametaphosphate in 1 litre distilled deionized water and 52.0 g sodium hydroxide in one litre distilled deionized water. Mix 100 ml of each solution daily.

7.2.2. Buffer solution: Dissolve 89.7 g disodium hydrogen phosphate hydrated and 10.0 g disodium hydrogen phosphate in distilled deionized water and dilute to five litres.

7.2.3. Hypochlorite stock solution: Dilute 100 ml Javex to 500 ml with distilled deionized water and filter through a 0.45-micron filter.

7.2.4. Hypochlorite reagent solution: Transfer 5 ml hypochlorite stock solution to a 1-litre volumetric flask and dilute to 1 litre with distilled deionized water.

7.2.5. Reducing agent: Dissolve 40.0 g oxalic acid and 340.0 g monochloracetic acid in distilled deionized water and dilute to two litres.

7.2.6. Ortho-tolidine: Prepare by heating 1.2 g 0-tolidine dihydrochloride in 120 ml conc hydrochloric acid, HCl, at 60°C for 1 hr; then adjust to a volume of 1 litre with distilled water.

7.2.7. Standard ammonia solutions: See ammonia method (automated) described elsewhere in this manual.

8. Procedure

8.1. The sample tray (sampler 11) is filled with samples and standards and covered with saran wrap to prevent contamination from the atmosphere.

8.2. The probe used with the sampler is a metallic needle type that pricks the saran wrap to withdraw samples.

8.3. Samples and standards are run at a rate of 20/hr.

8.4. Run the samples and standards using the manifolds shown in Figures 9, 10 and 11 as follows:

8.4.1. Figure 9 shows the flow diagram for total soluble nitrogen and involves the oxidation of organic nitrogenous compounds by UV - irradiation to a mixture of nitrate and nitrite and the measurement of the resultant mixture formed.

8.4.2. Figures 10 and 11 are the flow diagrams for nitrate + nitrate and ammonia, respectively. These manifolds are essentially the same as those detailed elsewhere in this manual except that two additional lines containing acid and alkali have been added to simulate the addition of these chemicals used in Figure 9 for the determination of total organic nitrogen.

9. Calculations

9.1. Prepare calibration curves for nitrate + nitrite and ammonia without irradiation and for total nitrogen after irradiation derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentrations in the samples of nitrate + nitrite and ammonia without irradiation and for total nitrogen after irradiation by comparing sample peak heights with the calibration curves.

9.3. Determine the concentration of organic nitrogen by subtracting the concentration of nitrate + nitrite and ammonia obtained without irradiation from the total nitrogen content obtained after irradiation.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a concentration of 200 ug/l organic nitrogen - N was ±2.02%.

11. Reference

11.1. Afghan, B.K., P.D. Goulden and J.F. Ryan. An Automated Method for Determination of Soluble Nitrogen in Natural Waters. Paper presented at Technicon Symposium, New York, Nov. 1970.

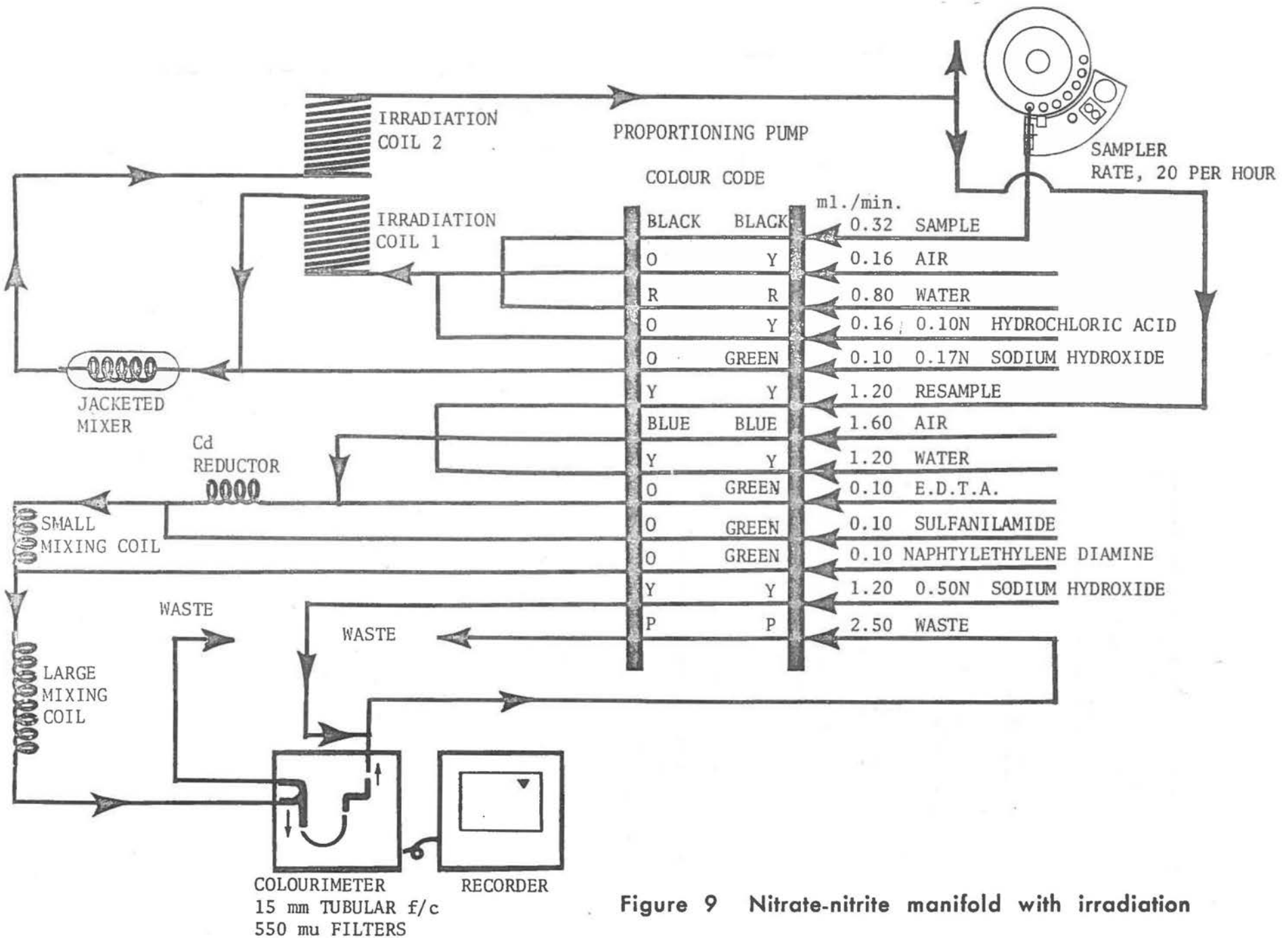

Figure 9 Nitrate-nitrite manifold with irradiation

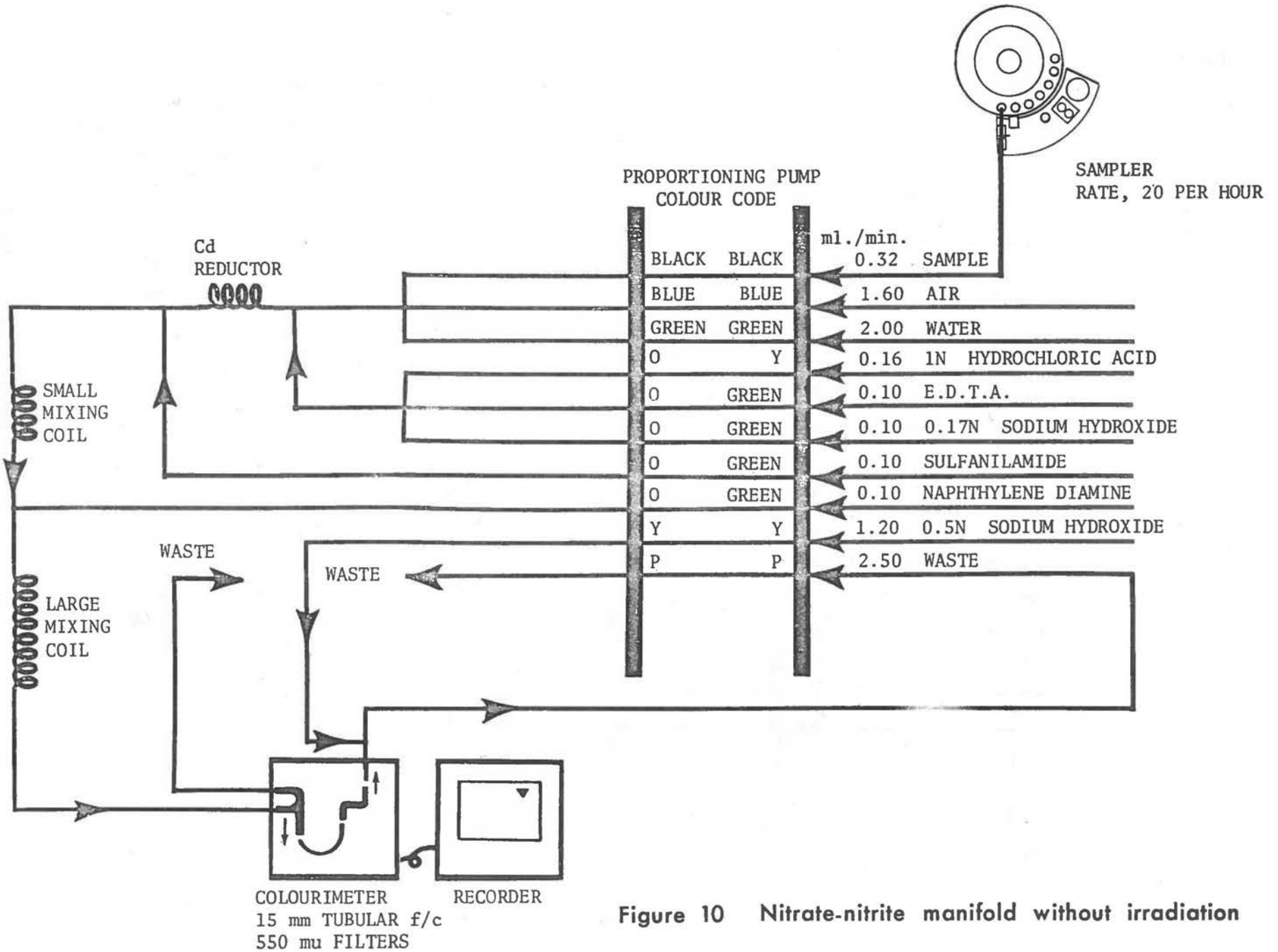

Figure 10 Nitrate-nitrite manifold without irradiation

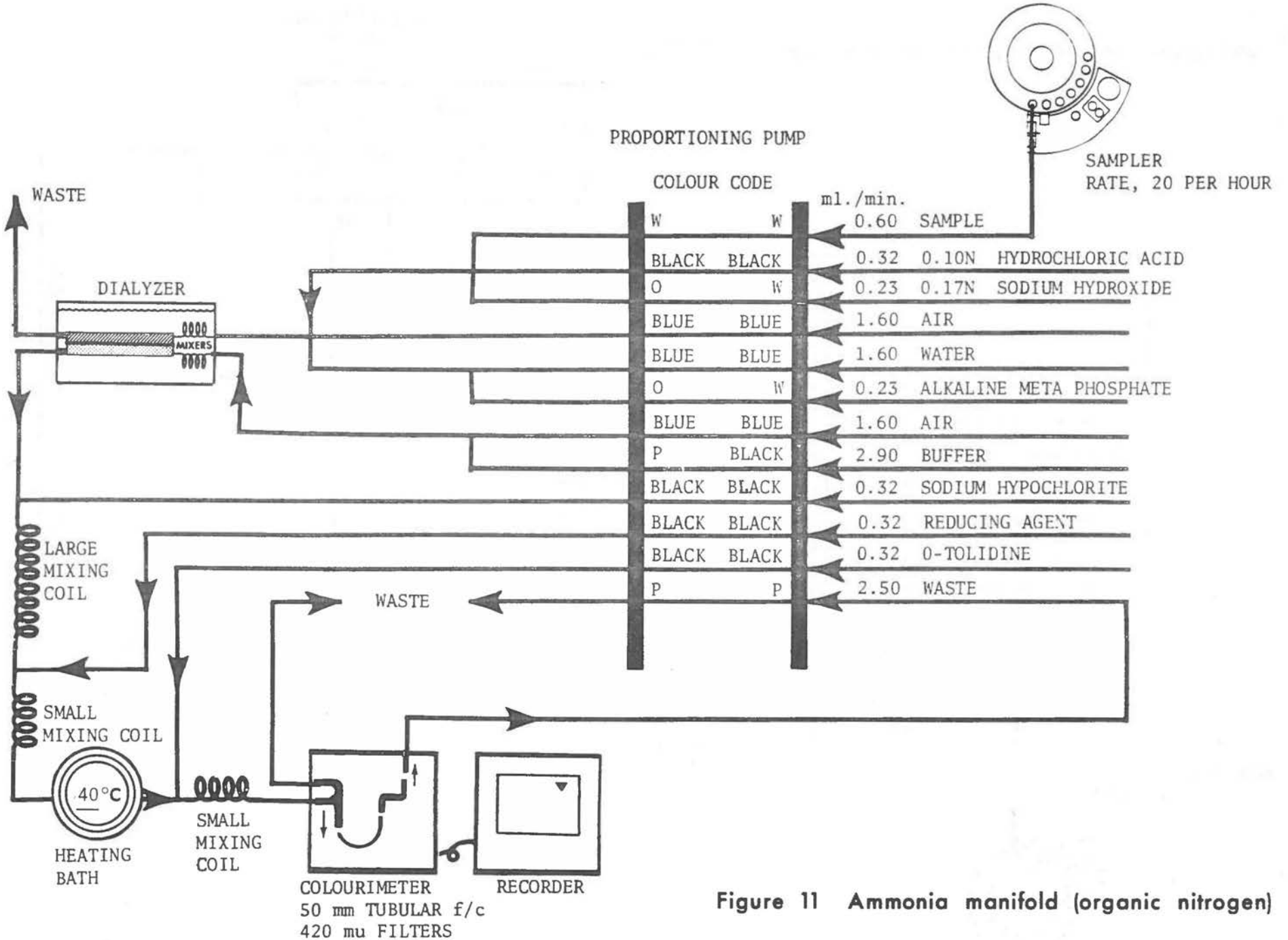

Figure 11 Ammonia manifold (organic nitrogen)

NITROGEN, TOTAL KJELDAHL AND ORGANIC

1. Scope and Application

1.1. This method is applicable to the determination of total Kjeldahl nitrogen in surface waters, wastes and saline waters. Concentrations of Kjeldahl nitrogen greater than 0.5 mg/l N may be accurately determined while values which fall below this value are questionable.

1.2. Levels of total Kjeldahl nitrogen less than 0.5 mg/l N should be determined using the ultra-violet digestion procedure described elsewhere in this manual.

2. Principle of Method

2.1. Definitions

2.1.1. Total Kjeldahl nitrogen: The sum of the free ammonia and organic nitrogen compounds which are converted to ammonium bisulphate under the conditions of digestion described below.

2.1.2. Organic nitrogen: The difference obtained by subtracting the free ammonia value from the total Kjeldahl nitrogen value. Organic nitrogen may be determined directly by removal of the ammonia before the digestion step.

2.2. In the presence of sulphuric acid, potassium sulphate, and mercuric sulphate (the latter as a catalyst), nitrogen of many organic materials is converted to ammonium bisulphate. The ammonia is distilled from an alkaline medium and absorbed in boric acid. The ammonia is then determined by titration with standard sulphuric acid, using a mixed indicator.

3. Interference

3.1. Nitrogen compounds from outside sources will cause high result.

4. Sampling Procedure and Storage

4.1. Samples should be analysed within 24 hours of sampling because conversion of organic nitrogen to ammonia may occur.

5. Sample Preparation

5.1. Shaken samples are used for this test.

6. Apparatus

6.1. Kjeldahl apparatus, combination digestion and distillation unit available from Labcanco Corp.

6.2. Kjeldahl flasks, 800-ml capacity.

7. Reagents

7.1. Phosphate buffer solution, 0.5 M: Dissolve 14.3 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 68.8 g anhydrous dipotassium hydrogen phosphate, K_2HPO_4, in distilled water and dilute to 1 litre.

7.2. Mercuric sulphate solution: Dissolve 8 g red mercuric oxide, HgO, in 50 ml 1 + 5 H_2SO_4 and dilute to 100 ml with distilled water.

7.3. Sulphuric acid - mercuric sulphate - potassium sulphate solution: Dissolve 267 g potassium sulphate, K_2SO_4, in 1,300 ml distilled water and add 400 ml conc H_2SO_4. Add 50 ml mercuric sulphate solution and dilute to 2 litres. This reagent crystallizes at temperature lower than 14°C.

7.4. Sodium hydroxide - sodium thiosulphate solution: Dissolve 500 g sodium hydroxide, NaOH, and 25 g sodium thiosulphate, $Na_2S_2O_3.5H_2O$, in distilled water and dilute to 1 litre.

7.5. Phenolphthalein indicator solution: Dissolve 5 g phenolphthalein disodium salt in distilled water and dilute to 1 litre. If necessary, add 0.02 N NaOH drop-by-drop until a faint pink colour appears

7.6. N-Point indicator solution: (Especially made for Kjeldahl test; available from Matheson Coleman and Bell Manufacturing Chemists, Norwood, Ohio).

7.7. Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in distilled water and dilute to 1 litre. Make fresh every 30 days.

7.8. Standard sulphuric acid titrant, 0.02 N: In this strength, 1.00 ml = 0.28 mg N.

7.9. Sulphuric acid, H_2SO_4, conc.

8. Procedure

8.1. Place measured sample into an 800-ml Kjeldahl flask. The sample size can be determined from the following table:

Organic Nitrogen in Sample mg/l N	Sample Size ml
0 - 5	500
5 - 10	250
10 - 20	100
20 - 50	50.0
50 - 100	25.0

Dilute the sample to 500 ml, if necessary.

8.2. If organic nitrogen is to be determined, proceed with step 8.3. If total Kjeldahl nitrogen is to be determined, omit step 8.3 and proceed with step 8.4.

8.3. Add 25 ml phosphate buffer solution (7.1) and boil off the free ammonia (boil to about 1/3 the original volume). Let cool.

8.4. Add 50 ml acid-sulphate solution (7.3) and evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colourless; continue boiling for an additional 20 min. Cool the residue and add 300 ml distilled water.

8.5. Make alkaline by careful addition (approximately 50 ml) of sodium hydroxide-thiosulphate solution (7.4) without mixing by slowly pouring the caustic solution down the neck of the digestion flask while holding the flask in a tilted position. Do not mix until the digestion flask has been connected to the distillation apparatus as ammonia may be lost.

8.6. Connect the Kjeldahl flask to the distillation apparatus with the tip of the condenser below the level of the boric acid solution in the receiving flask.

8.7. Distill into 50 ml boric acid solution (7.7) until about 200 ml distillate has been collected.

8.8. Titrate the distillate with 0.02 N H_2SO_4(7.8) using 0.5 ml of indicator until the indicator turns pinkish brown. Run a blank using distilled water instead of sample and carry through the procedure.

9. Calculation

9.1. Depending on the procedure used, calculate either the total Kjeldahl nitrogen or organic nitrogen in the sample as follows:

$$\text{mg/l N} = \frac{(A-B) \times N \times 14{,}000}{C}$$

where A = ml H_2SO_4 for sample,
B = ml H_2SO_4 for blank,
C = ml sample,
N = normality of sulphuric acid solution.

9.1.1. If the normality of the sulphuric acid solution is exactly 0.02 N the formula is shortened to:

$$\text{mg/l N} = \frac{(A-B) \times 280}{C}$$

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a total Kjeldahl nitrogen concentration of 25 mg/l N was ±4.58%.

11. References

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.2. Federal Water Pollution Control Administration, 1969. FWPCA Methods for Chemical Analysis of Water and Wastes, U.S. Department of the Interior, Cincinnati, Ohio.

OXYGEN CONSUMED

1. Scope and Application

1.1. The oxygen-consumed determination is a measure of the readily oxidizable material in a water and is applicable to surface waters with less than 1000 mg/l chloride.

2. Principle of Method

2.1. An acidified sample is digested with potassium permanganate in a boiling-water bath for 30 minutes, during which time reducing substances are oxidized along with part of the carbonaceous material. The remaining permanganate is reacted with a volume of oxalate equivalent to the permanganate originally added, and the excess oxalate is determined by back titration with permanganate. The permanganate required in the back titration is equivalent to the oxygen consumed.

3. Interferences

3.1. Not all organic matter can be oxidized completely by this method and some inorganic substances, notably chloride, can react partially with permanganate.

3.2. Chlorides in excess of 1,000 mg/l Cl will give high results.

4. Sampling Procedure and Storage

4.1. Sampling bottle should be tightly capped and stored in places far away from organic materials.

5. Sample Preparation

5.1. If the sample is cloudy, allow particles to settle out by standing. Take supernatant liquid for analysis.

6. Apparatus

6.1. Conical flask, 300-ml capacity.

6.2. Water bath, boiling.

6.3. Stopwatch.

7. Reagents

7.1. Dilute H_2SO_4, 25%: Cautiously, add 250 ml conc H_2SO_4 with stirring to 500 ml distilled water and dilute to 1 litre.

7.2. Sodium oxalate standard solution, (.0125 N): Dry reagent grade sodium oxalate, $Na_2C_2O_4$, at 105°C overnight and store in a desiccator. Dissolve 0.8374 g dried material in distilled water and make up to 1 litre with distilled water.

7.3. Potassium permanganate stock solution: Dissolve 4.0 g potassium permanganate, $KMnO_4$, in 1 litre distilled water; filter.

7.4. Potassium permanganate standard solution: Dilute 100 ml stock solution (7.3) to 1 litre with distilled water. This solution is standardized against 10 ml hot oxalate solution.

8. Procedure

8.1. Pipette a 25-ml sample into a 300-ml conical flask and dilute to 100 ml with distilled water.

8.2. Add 10 ml H_2SO_4 solution. (7.1)

8.3. Add 10 ml standard permanganate solution (7.4): mix by swirling.

8.4. Place the flask in a boiling-water bath and digest for 30 min. The flask must be at such depth that the surface of the sample is below the surface of the boiling water throughout the digestion period.

8.5. Remove the flask from the bath and cool to about 70°C.

8.6. Add 10.0 ml standard oxalate solution (7.2), and mix.

8.7. Titrate the hot solution with standard permanganate until a faint pink end point is obtained and record volume of permanganate used.

8.8. Carry out a blank on 25 ml distilled water treated the same as the sample.

9. Calculations

9.1. Calculate the oxygen consumed in mg/l as follows:

9.1.1. $$\text{mg/l oxygen consumed} = \frac{NX(A-B) \times 8000}{\text{ml sample}}$$

where N = normality of $KMNO_4$,
A = ml titration for sample,
B = ml titration for blank.

9.1.2. If normality of $KMnO_4$ is 0.0125 and sample size is 25 ml, then calculation is:

$$\text{mg/l oxygen consumed} = 4.0\ (A-B).$$

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at an oxygen consumed level of 5.7 mg/l was ±7.23%.

11. Reference

11.1. Rainwater, F.H. and L.L. Thatcher, 1960. Methods for collection and analysis of water samples. United States Geological Survey Water-Supply Paper 1954.

OXYGEN DEMAND, BIOCHEMICAL (BOD)

1. Scope and Application

1.1. The methods described cover the measurement of biochemical oxygen demand of industrial water and industrial waste water.

2. Principle of Method

2.1. Biochemical oxygen demand (BOD) is defined as the quantity of oxygen required for biological and chemical oxidation of water-borne substances under conditions of test. A sample of water is incubated at 20°C for 5 days (See Note 1) under proper conditions. Comparison of dissolved oxygen content at the beginning and end of the incubation period provides a measure of the biochemical oxygen demand. The procedure used to determine BOD depends upon the nature of the sample and three methods are used as follows:

1. The direct method. With samples whose 5-Day BOD does not exceed 7 mg/litre, the BOD is determined by measuring the dissolved oxygen content of the water (after aerating to bring the dissolved oxygen level near saturation at the start of the test) before and after a standard incubation period of five days at 20°C.

2. Unseeded dilution method. With waters having BOD values greater than 7 mg/litre, appropriate sample aliquots are diluted using water saturated with oxygen (dilution water) and dissolved oxygen content determined immediately after dilution and after incubation.

3. Seeded dilution method. It is extremely important that conditions be suitable for the living organisms to function in an unhindered manner during the incubation. This condition means that toxic substances be absent and that all necessary nutrients such as nitrogen and phosphorus be present. Therefore, it is important that a mixed group of organism, commonly called "seed", be present in the test.

   In the seeded dilution method, the dilution water is seeded with the proper kind and number of organisms before the BOD test.

Note 1. For all practical purposes, the reaction is considered complete in 20 days; however, a 20-day period is too long to wait for results in many instances. It has been found by experience that a reasonably large percentage of the total BOD is exerted in 5 days; consequently the test has been developed on the basis of a 5-day incubation period.

It is strongly recommended that a period of 7 days be considered because the 5-day period makes scheduling of work difficult, since if the test is started Monday or Tuesday it requires attention on the following week-end. For certain wastes it may be advisable to determine the oxidation curve for conversion of data from one incubation period to another.

3. Interferences

3.1. Many synthetic organic components in industrial waste waters are not biodegradable without the seeding procedure because of either a toxic effect or a deficiency or absence of appropriate microorganisms.

3.2. Chlorine residuals must be removed prior to the test (for removal procedure, see Section 5, Sample Preparation).

3.3. Because waters that contain sulphide, sulphite, or ferrous ions create an immediate demand on the dissolved oxygen, it is necessary to distinguish this immediate dissolved oxygen demand (IDOD) from the true BOD. The depletion of DO in a standard water dilution of the sample in 15 min has been arbitrarily selected as the IDOD.

4. Sampling Procedure and Storage

4.1. The sample collected for BOD analyses should be protected from atmospheric oxygen and analyses started within 4 hours of collection.

5. Sample Preparation

5.1. Samples containing acidity or caustic alkalinity are neutralized to approximately pH 7 with H_2SO_4 (1N) or NaOH (1N) using a pH meter.

5.2. Chlorine residuals, if present in a sample, may dissipate after 1-2 hours, then the dilution method may be used. If chlorine residuals do not dissipate on standing, the neutralized sample must be treated with 0.025 N sodium sulphite solution. The appropriate quantity of sodium sulphite solution is determined on a 100 to 1,000-ml portion of the sample by adding 10 ml 1 + 1 acetic acid or 1 + 50 H_2SO_4, followed by 10 ml potassium iodide solution (10 g in 100 ml) and titrating with 0.025 N sodium sulphite solution to the starch-iodide endpoint. Add to a volume of sample the quantity of sodium sulphite solution determined by the above test; mix, and after 10-20 min, test sample aliquots for residual chlorine to check the treatment.

5.3. Samples supersaturated with oxygen. This situation may occur during winter or during algal blooms. The dissolved oxygen content must be reduced to saturation (9.17 mg/l at 20°C) by aerating with compressed air or by vigorous shaking of sample container.

6. Apparatus

6.1. Incubation bottles, 300-ml bottles with ground-glass stoppers.

6.2. Incubator, thermostatically controlled at 20°C ±1°C. All light should be excluded to prevent formation of DO by algae in the sample.

7. Reagents

7.1. Distilled water: Water used for solutions and for preparation of the dilution water must be of the highest quality, distilled from a block

tin or all-glass still, contain less than 0.01 mg/l copper, and be free of chlorine, chloramines, caustic alkalinity, organic material or acids.

7.2. Phosphate buffer solution: Dissolve 8.5 g potassium dihydrogen phosphate, KH_2PO_4; 21.75 g dipotassium hydrogen phosphate, K_2HPO_4; 33.4 g disodium hydrogen phosphate heptahydrate, $Na_2HPO_4.7H_2O$; and 1.7 g ammonium chloride, NH_4Cl, in about 500 ml distilled water and dilute to 1 litre. The pH of this buffer should be 7.2 without further adjustment. If dilution water is to be stored in the incubator, the phosphate buffer should be added just prior to using the dilution water.

7.3. Magnesium sulphate solution: Dissolve 22.5 g magnesium sulphate, $MgSO_4.7H_2O$, in distilled water and dilute to 1 litre.

7.4. Calcium chloride solution: Dissolve 27.5 g anhydrous calcium chloride $CaCl_2$, in distilled water and dilute to 1 litre.

7.5. Ferric chloride solution: Dissolve 0.25 g ferric chloride, $FeCl_3.6H_2O$, in distilled water and dilute to 1 litre.

7.6. Acid and alkali solutions, 1N. For neutralization of waste samples which are either caustic or acidic.

7.7. Sodium sulphite solution, 0.025 N: Dissolve 1.575 g anhydrous sodium sulphite, Na_2SO_3, in 1 litre distilled water. This solution is not stable and should be prepared daily.

7.8. Seeding material. Satisfactory seed may sometimes be obtained by using the supernatant liquor from domestic sewage which has been stored at 20°C for 24-36 hr. Refer to ASTM (Ref. 11.2) for a more detailed explanation of seeding material.

7.9. Preparation of dilution water: The distilled water used should have been stored in cotton-plugged bottles for a sufficient length of time to become saturated with DO. The water may also be aerated by shaking a partially filled bottle or using a supply of clean compressed air. Situations may be encountered where it is desired to use stabilized river water to check stream performance with laboratory procedure. The distilled water used should be as near as possible to 20°C and of the highest purity. Place the desired volume of distilled water in a suitable bottle and add 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride, and ferric chloride solutions for each litre of water.

7.9.1. Seeding: If necessary, the dilution water is seeded by using the seed found to be the most satisfactory for the particular waste under study. Only past experience can determine the actual amount of seed to be added per litre. Seeded dilution water should be used the same day it is made.

8. Procedure

8.1. Direct Method

8.1.1. Fill two BOD bottles with the sample. Be sure that no air bubbles are entrapped and that the bottles are filled to overflowing when the stoppers are inserted.

8.1.2. Determine the dissolved oxygen concentration in one of the bottles using the procedure outlined elsewhere in this manual. Record the value as "Initial DO".

8.1.3. Allow the other bottle to incubate for five days and then determine the dissolved oxygen content. Record value as "Final DO".

8.2. Unseeded Dilution Method

8.2.1. Conduct pre-treatment as necessary.

8.2.2. A range of dilutions is desirable, and a dilution in the range 40-90% of the original dissolved oxygen content will give the best results. At least 3 dilutions should be prepared.

8.2.3. Carefully siphon dilution water into a graduated cylinder of 1000 to 2000-ml capacity, filling the cylinder half full with no entrainment of air. Add the quantity of carefully mixed sample to desired dilution and dilute to the mark with dilution water. Mix well with a plunger-type mixing rod avoiding any entrainment of air.

8.2.4. Siphon, with continued mixing, the diluted sample to fill completely 3 BOD bottles; one for incubation, one for the determination of dissolved oxygen content, and the other for the determination of immediate dissolved oxygen demand (IDOD).

Note - Preparation of diluted samples may also be done by direct measurement of suitable amounts of sample into BOD bottles using a large tipped volumetric pipette and then filling the bottles with dilution water. Dilutions greater than 1:100 must be made by diluting the sample in a graduated cylinder before measurement into incubation bottle.

8.2.5. Determine the dissolved oxygen in one of the BOD bottles prepared above. Record as "Initial DO".

8.2.6. Incubate one of the other bottles for 15 min and determine the oxygen content after the incubation for calculation of the immediate oxygen demand (IDOD). Record result as DO after 15 min.

8.2.7. Incubate the remaining bottle for 5 days and then determine the oxygen content. Record as "Final DO".

8.3. Seeded Dilution Method

8.3.1. The procedure used in the unseeded dilution method is followed, but an additional step is necessary and that is to correct for the effect of the seed depletion of DO. Determine the oxygen depletion of the seed by setting up a separate series of seed dilutions

(controls) and selecting those resulting in a 40 to 70% depletion in 5 days. One of these depletions is then used to calculate the correction due to the small amount of seed in the dilution water.

9. Calculations

9.1. Calculate the immediate dissolved oxygen demand (IDOD) as follows:

$$\text{IDOD, mg/l} = (\text{Initial DO} - \text{DO after 15 min}) \frac{300}{\text{ml of sample per bottle}}$$

9.2. Seed correction. Calculate the seed corrections as follows:

$$\text{Seed correction} = \text{BOD of seed control} \times \frac{\text{\% seed in sample}}{\text{\% seed in control}}$$

9.3. Direct method. Calculate the BOD as follows:

$$\text{BOD, mg/l} = \text{Initial DO} - \text{Final DO}$$

9.4. Unseeded dilution method. Calculate the BOD as follows:

$$\text{BOD, mg/l} = (\text{DO after 15 min} - \text{Final DO}) \frac{300}{\text{ml of sample per bottle}}$$

9.5. Seeded dilution method. Calculate BOD as follows:

$$\text{BOD, mg/l} = (\text{DO after 15 min} - \text{Final DO-Seed Correction}) \frac{300}{\text{ml of sample per bottle}}$$

10. Precision and Accuracy

10.1. No data available.

11. References

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.2. American Society for Testing and Materials, 1966. Book of ASTM Standards Part 23: Industrial Water; Atmospheric Analysis. Philadelphia.

11.3. Martin, D.F. 1968. Marine Chemistry. Volume 1, Analytical Methods. Marcel Dekker Inc., New York.

OXYGEN DEMAND, CHEMICAL (COD)

1. Scope and Application

1.1. This procedure is applicable to surface waters and wastes in samples having a COD higher than 10 mg/l. COD Values below 10 mg/l may be used to indicate an order of magnitude.

2. Principle of Method

2.1. The method is based on the fact that most organic compounds can be oxidized by potassium dichromate under acid conditions. A sample is refluxed with known amounts of potassium dichromate and sulphuric acid, and the excess dichromate is titrated with ferrous ammonium sulphate. The amount of oxidizable organic matter is proportional to the potassium dichromate consumed.

3. Interferences

3.1. Traces of organic material from glassware or other sources in the laboratory will cause positive errors.

4. Sampling Procedure and Storage

4.1. No special precautions.

5. Sample Preparation

5.1. Sample should be either well shaken or blended to permit representative sampling for analysis.

6. Apparatus

6.1. Reflux apparatus, consisting of 300-ml conical flask with ground-glass stoppers, 24/40 neck connected to a 300-mm Liebig or similar condenser with a 24/40 ground-glass joint.

6.2. Hot plate with sufficient power to insure adequate boiling of the contents of the refluxing mixture.

7. Reagents

7.1. Standard potassium dichromate solution, 0.250 N: Dissolve 12.259 g potassium dichromate, $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for 2 hours, in distilled water and dilute to 1 litre. To eliminate the interference of nitrites, sulphamic acid, in the amount of 10 mg for every 1 mg of nitrite N in the refluxing flask, may be added to the dichromate solution. Thus 0.12 g of sulphamic acid per litre of dichromate solution will eliminate the interference of nitrites up to 6 mg/l in the sample.

7.2. Standard potassium dichromate solution, 0.025 N: Dilute 100 ml solution 7.1 to 1 litre with distilled water.

7.3. Sulphuric acid reagent: conc H_2SO_4 containing 22 g silver sulphate, Ag_2SO_4, per 9-lb bottle (1 or 2 days required for dissolution).

7.4. Standard ferrous ammonium sulphate titrant, 0.25 N: Dissolve 98 g ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, in distilled water. Add 20 ml of conc H_2SO_4 (caution!); cool, and dilute to 1 litre. This solution must be standardized against $K_2Cr_2O_7$(7.1) daily.

7.4.1. Standardization of ferrous ammonium sulphate: Dilute 10.0 ml standard potassium dichromate solution (7.1) to about 100 ml. Add 30 ml conc H_2SO_4 (caution!) and allow to cool. Titrate with the ferrous ammonium sulphate titrant (7.4), using 2 or 3 drops of ferroin indicator.

$$\text{Normality} = \frac{\text{ml } K_2Cr_2O_7 \text{ X } 0.25}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

7.5. Standard ferrous ammonium sulphate, 0.025 N: Dilute 100 ml ferrous ammonium sulphate 0.25 N (7.4) to 1 litre with distilled water. This solution must be standardized daily against the standard potassium dichromate solution, 0.025 N (7.2) following the same procedure as the standardization of the ferrous ammonium sulphate titrant, 0.25 N (7.4).

7.6. Ferroin indicator solution: Ferroin can be prepared by dissolution of 1.485 g 1,10-phenanthroline monohydrate and 0.695 g ferrous sulphate, $FeSO_4.7H_2O$, in water and dilute to 100 ml. Alternatively, this indicator can be purchased already prepared.

7.7. Silver sulphate, Ag_2SO_4, reagent powder.

7.8. Mercuric sulphate, $HgSO_4$, analytical grade crystals.

8. Procedure

8.1. Place 0.4 g $HgSO_4$ in a refluxing flask. Add 20.0-ml sample or an aliquot diluted to 20.0 ml with distilled water, and mix, (0.4 g $HgSO_4$ is sufficient to complex 40 mg chloride ion. If more chlorides are present in the sample, add more $HgSO_4$ to maintain a $HgSO_4$:Cl ratio of 10:1).

8.2. Then add 10.0 ml $K_2Cr_2O_7$ solution (7.1) followed by careful addition of 30 ml conc H_2SO_4 containing Ag_2SO_4 (7.3) with mixing. (Caution: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser).

8.3. Pumice granules or glass beads should be added to the reflux mixture to prevent bumping.

8.4. Attach the flask to the condenser and reflux the mixture for 2 hrs.

8.5. Cool and wash down the condenser with distilled water.

8.6. Dilute the mixture to about 100 ml, cool to room temperature, and titrate excess dichromate with standard ferrous ammonium sulphate (7.4) using 2 or 3 drops of ferroin indicator (7.6). Be consistent with the quantity of ferroin used on sequential samples. The end point is indicated by a color change from blue-green to reddish-brown.

8.7. For blank determination, use 20 ml distilled water instead of the sample and proceed in manner as described above.

8.8. If samples low in COD are to be analysed, the same procedure is to be followed with 2 exceptions, as follows:

(1) 0.025 N potassium dichromate is used, and

(2) the back-titration is performed with 0.025 N ferrous ammonium sulphate (7.5).

9. Calculations

9.1. Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/l} = \frac{(a-b)c \times 8{,}000}{\text{ml sample}}$$

where COD = Chemical oxygen demand from dichromate
a = ml $Fe(NH_4)_2 (SO_4)_2$ used for blank
b = ml $Fe(NH_4)_2 (SO_4)_2$ used for sample
c = normality of $Fe(NH_4)_2 (SO_4)_2$

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a COD concentration of 40.0 mg/l was ±6.60%.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

OXYGEN, DISSOLVED

(Azide Modification of Iodometric Method)

1. Scope and Application

1.1. This titration method is applicable to the determination of dissolved oxygen in surface waters and many wastewaters. (See interferences below).

2. Principle of Method

2.1. The sample is treated with manganous sulphate and a strongly alkaline iodide reagent. The manganous hydroxide formed reacts with the dissolved oxygen in the sample to form a brown precipitate, manganic hydroxide, $MnO(OH)_2$. Upon acidification, in the presence of iodide, iodine is liberated to an amount equivalent to the dissolved oxygen originally present. The iodine is then titrated with standard sodium thiosulphate.

3. Interferences

3.1. The method is not applicable under the following conditions:

3.1.1. Samples containing more than 1 mg/l of ferrous iron.

3.1.2. Samples containing sulphite, thiosulphite, polythionate, free chlorine or hypochlorite.

3.1.3. Samples high in suspended solids.

3.1.4. Samples containing other oxidizing or reducing materials.

3.2. If 1 ml fluoride solution is added before acidifying the sample and there is no delay in titration, the method is also applicable in the presence of 100-200 mg/l ferrous iron.

3.3. In instances where the azide modification is not applicable a DO probe should be used.

4. Sampling Procedure and Storage

4.1. Collect the sample, if possible, in a 300-ml BOD bottle, taking precaution to avoid entrainment or dissolution of atmospheric oxygen.

4.2. Where samples need be collected using other type samplers, such as Knudsen bottles, the BOD bottle should be filled from the sampler within 15 minutes of sampling.

5. Sample Preparation

5.1. To fill the BOD bottle, a length of flexible tubing should be attached to the outlet of the sampler and the tubing extended to the bottom of the BOD bottle. Care must be taken to prevent turbulence and air-entrainment, especially when just starting to fill the bottle. Keep the end of the tubing in the BOD bottle under the surface of the water while the bottle is filling. Allow the water to overflow from the top of the BOD bottle and replace the stopper at once. The sample is ready for oxygen determination.

6. Apparatus

6.1. 300-ml BOD (biological oxygen demand) bottles.

6.2. 100-ml automatic pipette with a two-way stopcock (Scientific Glass Apparatus Co., # JP-6000).

6.3. Vacuum system. A small laboratory pump such as Cole-Parmer Instrument and Equipment Co. Roll-Flex Pump 7022.

6.4. 10-ml burette with graduations every 0.05 ml and with automatic zero adjust.

6.5. 250-ml Erlenmeyer flasks painted white on the outside over the base and two-thirds of the way around the sides. During the titrations, illuminate the flask through the unpainted portion of the side by means of an ordinary light bulb and stir the contents of the flask with a white magnetic stirring bar.

6.6. Lamp and stand suitable for titrations.

6.7. Magnetic stirrer and white stirring bars.

7. Reagents

7.1. Manganous sulphate solution: Dissolve 365 g manganous sulphate monohydrate, $MnSO_4.H_2O$, or 400 g manganous sulphate dihydrate, $MnSO_4.2H_2O$, or 480 g manganous sulphate tetrahydrate, $MnSO_4.4H_2O$ in freshly boiled distilled water and dilute to one litre. A magnetic stirrer will speed up solution. Store in a glass bottle.

7.2. Alkaline-iodide-azide solution: Dissolve 400 g sodium hydroxide pellets, NaOH, in 500 ml of freshly boiled distilled water. (Add the sodium hydroxide in small increments and dissolve each addition before proceeding). Then add 900 g sodium iodide, NaI, while the solution is still hot. Dissolve 10 g sodium azide, NaN_3, in 40 ml distilled water. Add the latter to the former and dilute, if necessary to 1 litre.

7.3. Sulphuric acid, concentrated.

7.4. Sodium thiosulphate solution, 0.0187N, 1 ml = 1.5 mg DO. (The thiosulphate concentration is such that 10 ml are required for an oxygen concentration of 15.5 mg/l, near the maximum value to be found

in waters such as the Great Lakes): Dissolve 4.8 g sodium thiosulphate pentahydrate, $Na_2S_2O_3.5H_2O$; and 0.1 g sodium carbonate, Na_2CO_3, in one litre of distilled water. Add a few drops of chloroform as a preservative.

7.4.1. Standardization Procedure: Fill a BOD bottle with water (not chlorinated tap water). Add 1.0 ml alkaline-iodide-azide reagent, replace the stopper, and mix. Add 1.0 ml concentrated sulphuric acid and mix. Add 1.0 ml manganous sulphate and mix again. Transfer 100 ml of solution from the BOD bottle to an Erlenmeyer flask and add 10.00 ml potassium bi-iodate (7.6). Let the solution stand for at least two minutes in the dark, then titrate the liberated iodine with thiosulphate. (See section 8, Procedure, for details of titration).

Normality (N) of thiosulphate is obtained from the expression

$$N_1 \times V_1 = N_2 \times V_2$$

where N_1 = normality of sodium thiosulphate,
V_1 = volume of thiosulphate,
N_2 = normality of the standard bi-iodate solution,
V_2 = volume of potassium bi-iodate solution. (This is always 10.0).

7.5. Starch indicator solution: Add 30 g soluble starch to 1 litre of glycerol. Heat the mixture to 180°C and maintain that temperature until the solution is transparent.

7.6. Potassium bi-iodate, 0.01N: Dry a suitable amount of primary standard grade bi-iodate, $KH(IO_3)_2$, at 105°C for an hour. After cooling in desiccator weigh out 0.3249 g and dissolve in distilled water. Dilute to 1 litre and store this solution in a tightly stoppered dark glass bottle.

7.7. Potassium fluoride solution: Dissolve 40 g $KF.2H_2O$ in distilled water and dilute to 100 ml.

8. Procedure

8.1. Remove stopper from the BOD bottle and add, by means of pipettes placed just below the water in the BOD bottle, 1.0 ml of manganous sulphate reagent followed immediately by 1.0 ml of alkaline-iodide-azide solution. Restopper the bottle at once and mix the contents by shaking vigourously for at least 20 seconds or until the precipitated manganous and manganic hydroxide is evenly dispersed. No air bubbles should be trapped in the bottle.

8.2. After 2 to 3 minutes, shake the bottle again. Allow the precipitate in the sample to settle at least one-third the way down the bottle (about one hour required).

Note: The sample may be allowed to stand indefinitely at this stage as long as air is not drawn into the bottle.

8.3. Add 1.0 ml conc H_2SO_4 by placing the pipette just beneath the surface. Restopper the bottle and shake until dissolution of precipitate.

8.4. By means of the two-way pipette and vacuum system, transfer 100 ml of solution from the BOD bottle to a specially-painted Erlenmeyer flask containing a magnetic stirring bar.

8.5. Titrate at once with thiosulphate solution until the solution has a very pale straw colour. Then add four drops of starch solution. Continue the titration until the blue colour just disappears.

9. Calculations

9.1. Calculate the dissolved oxygen content of the sample as follows:

$$\text{Mg/l DO} = \frac{N \times V \times 8 \times 1000}{\text{ml sample titrated}}$$

where N = normality of sodium thiosulphate solution.
V = volume of sodium thiosulphate for sample.

Note: The volume of treated sample is 100 ml, but the volume of the water sample titrated is $100 \times \frac{(300-2)}{300}$, i.e., 99.3.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a dissolved oxygen concentration of 4.1 mg/l was ± 1.8%.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater, Twelfth Ed., New York.

1. Scope and Application

1.1. This electrometric measurement is applicable to all waters and over the whole pH scale. The pH of most natural waters falls within the range 4 to 9.

2. Principle of Method

2.1. The glass electrode in combination with a reference potential provided by a saturated calomel electrode is used for pH measurement. The active element of a glass electrode is a membrane of a special glass. The membrane forms a partition between two liquids of differing hydrogen ion concentration and a potential is produced between the two sides of the membrane that is proportional to the difference in pH between the liquids.

3. Interferences

3.1. High sodium concentrations at a pH above 10 interfere with the measurement. Corrections for the sodium error may be made by consulting a chart that may be supplied by the manufacturer of the electrodes being used.

4. Sampling Procedure and Storage

4.1. Plastic sample containers should be used and tightly sealed as soon as the sample has been collected. There should be no delay of pH measurement after the sample container has been opened and the sample reaches room temperature.

5. Sample Preparation

5.1. The sample should be brought to the laboratory temperature (±2°C) before pH measurement.

6. Apparatus

6.1. pH meter such as Radiometer general purpose Model 28 or equivalent.

6.2. Glass electrode.

6.3. Reference electrode (saturated calomel).

6.4. Magnetic stirrer and stirring bars.

7. Reagents

7.1. Standard pH buffer solutions: Dry powders are available from suppliers of pH meters.

8. Procedure

8.1. Closely follow the procedure for setting up the instrument and preparing electrodes provided by the manufacturer.

8.2. Set temperature compensator to the temperature of the sample being measured. Buffers should also be at the same temperature as sample.

8.3. For standardizing, select two different buffer solutions in the approximate pH range of the samples to be measured.

8.4. Place a buffer solution into a beaker and, while gently stirring, place electrodes in the solution; wait until meter needle stabilizes and set calibration control to the correct value of the buffer.

8.5. Repeat (8.4) with the other buffer. The reading should be within 0.1 pH units.

8.6. Electrodes should be rinsed with distilled water and dried gently with soft wipers.

8.7. To determine pH of sample, place electrodes into a beaker containing sample while sample is being gently stirred. Wait until the meter needle stabilizes and record pH.

9. Calculations

9.1. pH meter reads directly in pH units.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at pH values of 8.8 and 4.0 were 0% at both levels, with values reported to nearest 0.1 pH units.

11. Reference

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

PHENOL

(Automated, Colourimetric 4-aminoantipyrine Method)

1. Scope and Application

1.1. This automated, colourimetric method can be used on fresh surface water samples for the estimation of phenol and of its ortho and meta substituted derivatives in the range 2 to 100 ug/l, provided these are steam-distillable.

1.2. The method can be used for analyses on sea water samples by slight modifications to the method that are detailed below.

2. Principle of Method

2.1. The phenols are removed from the water sample aliquot by steam distillation under acid conditions and collected in alkali at a pH of 10, using an ammonium hydroxide/ammonium chloride buffer. A red colour is formed by the reaction of the phenol with 4-aminoantipyrine under the oxidizing conditions provided by ammonium persulphate at a constant pH of 10.

3. Interferences

3.1. Strong oxidizing and reducing agents interfere with the colour-forming reaction and can degrade the phenol, as also can strong alkali.

3.2. Bacteria and other microorganisms can decompose the phenol in the sample.

3.3. Compounds associating with phenols in solution can hamper their steam distillation under acid conditions.

3.4. Steam-distillable, non-phenolic compounds (e.g., formaldehyde) which will also react with 4-aminoantipyrine to add to the phenol colour intensity of a water sample.

3.5. Sulphur compounds interfere with the colour-forming reaction.

4. Sampling Procedure and Storage

4.1. Owing to bacterial oxidation and to chemical oxidation, preservatives are required to maintain the original phenol concentration of the water sample. Thus, immediately on sample collection, the following steps should be carried out:

4.1.1. Fresh water samples: Add copper sulphate to a concentration of 1 g $CuSO_4.5H_2O$ per litre of sample, to inhibit bacterial degradation.

4.1.2. Acidify the sample with phosphoric acid, H_3PO_4, to a pH of less than 4, in order to ensure adequate copper ion activity and to liberate any dissolved hydrogen sulphide or sulphur dioxide.

4.1.3. Sea water samples: Add 10 ml acidified copper sulphate preservative solution (7.3) for each litre of sample. This will bring the pH to about 2 to 3, thus assuring adequate copper ion activity and also liberate any dissolved hydrogen sulphide or sulphur dioxide.

4.1.4. After preservative addition, for either fresh or sea waters, the samples should be stored in the dark at a temperature below 20°C and analysed within 24 hours of collection.

5. Sample Preparation

5.1. If much suspended matter is present, filtration through a glass fibre mat is required prior to filling the sample cups of the AutoAnalyzer.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler.

6.1.2. Two proportioning pumps.

6.1.3. Heating bath, 130°C and 120°C.

6.1.4. Fluoride micro-distillation head.

6.1.5. Two manifolds.

6.1.6. Colourimeter equipped with a 50 mm flow cell and 505 mu filters.

6.1.7. Recorder.

6.1.8. Two range expanders.

7. Reagents

N.B. These must be freshly prepared, daily, for best results.

7.1. 4-aminoantipyrine solution, 0.2%: Dissolve 2 g reagent in 1 litre of distilled water. To maintain a high pH, add 2 drops of conc NH_4OH solution/100 ml reagent solution.

7.2. Phosphoric acid solution, 10%: Dilute 100 ml conc phosphoric acid, H_3PO_4, to 1 litre with distilled water.

7.3. Acidified copper sulphate preservative solution: Dissolve 100 g copper sulphate, $CuSO_4.5H_2O$, in distilled water to which has been added 10 ml conc H_2SO_4. Dilute to 1 litre.

7.4. Ammonium persulphate solution, 2%: Dissolve 20 g ammonium persulphate, $(NH_4)_2S_2O_8$, in 1 litre of distilled water and maintain a pH greater than 8 by adding 2 drops of conc NH_4OH solution per 100 ml of reagent solution.

7.5. Ammonium chloride/ammonium hydroxide buffer solution, (pH = 10),: Dissolve 25 g ammonium chloride, NH_4Cl, in 50 ml conc ammonium hydroxide, NH_4OH, and make up to 1 litre with distilled water.

7.6. Stock phenol solution, 1000 mg/l: Dissolve 1 g phenol, C_6H_5OH, in 1 litre of distilled water and store in the dark. Prepare daily.

7.7. Standard phenol solutions: Prepare a series of standards, e.g., 100, 50, 25, 10, 6, 4, and 2 ug/l by diluting suitable aliquots of stock phenol solution to 1 litre with distilled water. Prepare daily.

8. Procedure

8.1. The manifold diagrams give the experimental details, Figure 12 for fresh water and Figure 13 for sea water samples. The differences between the 2 procedures are the omission of the 10% H_3PO_4 line, a lower bath temperature, and an increase in sample volume for the sea water procedure. These modifications to the fresh water procedure avoid bromide interference during sea water analyses and also prevent blockage by salt deposits.

8.1.1. Two range expanders, connected in series, are used to measure phenol concentrations down to 2 ug/l, when a total range expansion of up to 100 x can be employed. For phenol concentrations above 5 ug/l, one range expander is adequate.

8.1.2. A steady baseline drift may occur with a negative slope of about 6 chart units/hr. (equivalent to about 12 ug/l phenol/hr.) but this can be controlled by maintaining a high pH in the ammonium persulphate reagent solution with NH_4OH addition and maintaining a constant air temperature in the room.

8.1.3. The Tygon manifold tubing and the Acidflex for the phosphoric acid reagent should be changed daily for best results to maintain the baseline noise variation within ±0.5 chart unit, (equiv. to ±1 ug/l phenol at 40x range expansion.

8.1.4. Two proportioning pumps are used for each manifold. In each manifold, one pump is used for the distillation step while the other pump is used to hold the tubes necessary for the colour development on the sample after distillation.

9. Calculations

9.1. Prepare calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of phenol in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. Over the phenol concentration range of 0 to 100 ug/l the lower detection limit is about 2 ug/l. The precision of the method is ±1 ug/l over this range.

11. References

11.1. Regnier Z. and A.E.P. Watson, 1970. Procedure of the method developed in the Methods and Properties Section, Water Quality Division, Ottawa.

11.2. Technicon AutoAnalyzer Methodology, 1970. Industrial Method 51-69 W.

11.3. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.4. Water Research Association, 1966. "Notes on the Determination of Low Concentrations of Phenol in Water", Medmenham, England, T.I.R. No. 132, p. 1.

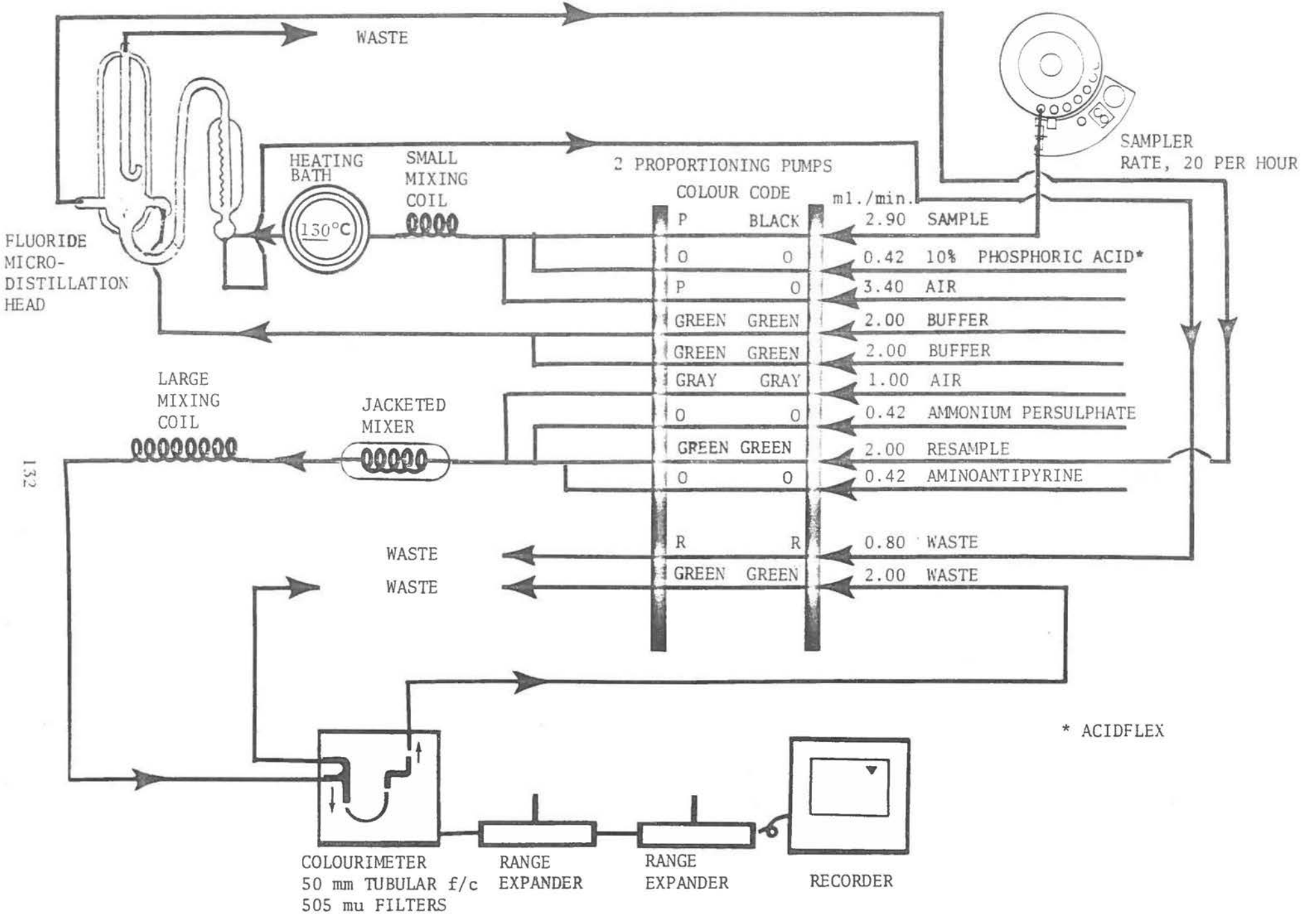

Figure 12 Phenol manifold - fresh water

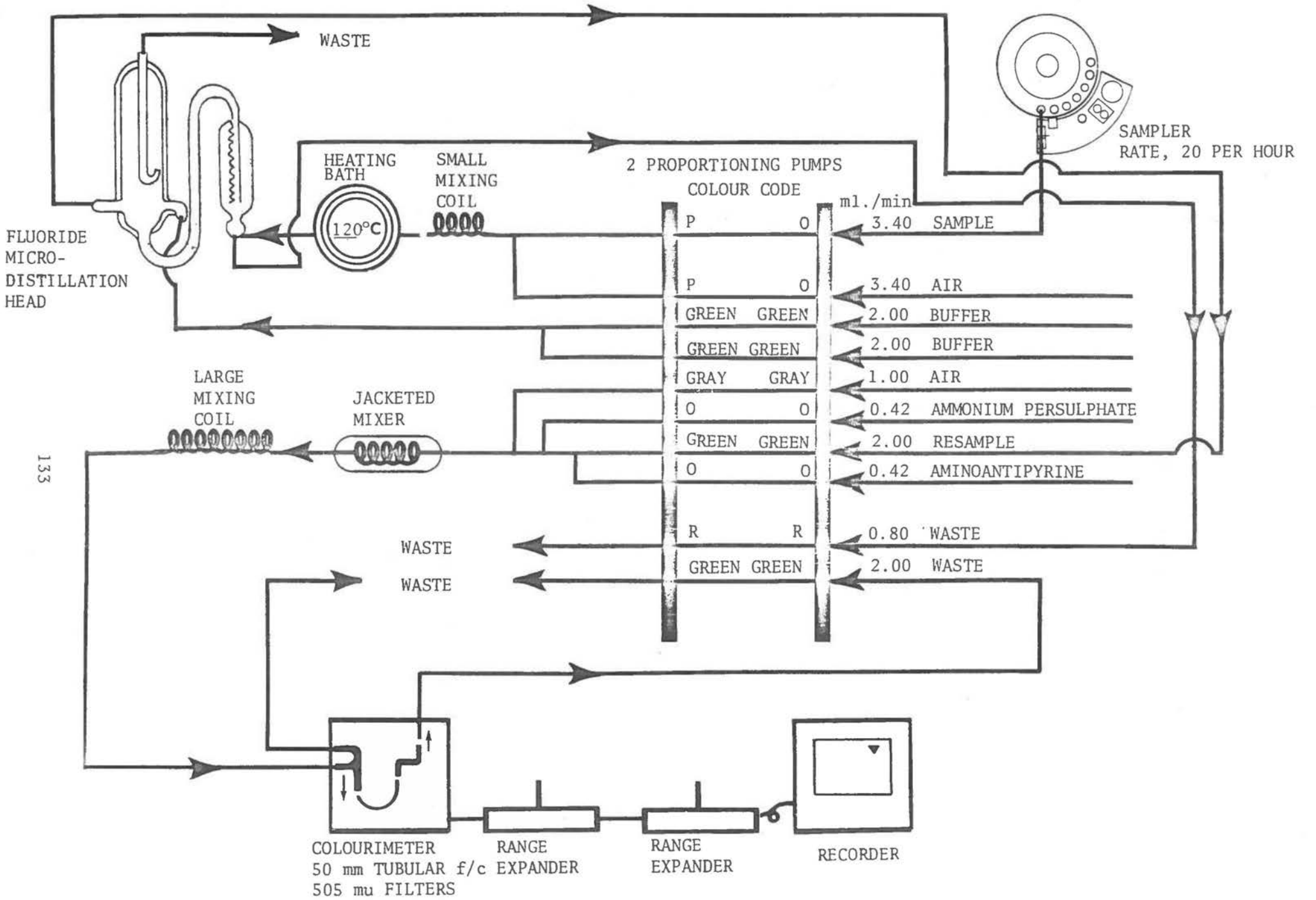

Figure 13 Phenol manifold - seawater

PHOSPHATE, INORGANIC

1. Scope and Application

1.1. This colourimetric method is applicable to surface and ground waters with inorganic phosphate levels in the range 5 to 200 ug/l (PO_4). Samples having higher concentrations than this can be measured by appropriate dilution of an aliquot.

2. Principle of the Method

2.1. The polyphosphates in a sample are hydrolyzed to orthophosphate by heating the sample in the presence of sulphuric acid. The resulting orthophosphate plus the orthophosphate originally present is then reacted with ammonium molybdate to form heteropoly molybdophosphoric acid. This is then reduced with stannous chloride in an aqueous sulphuric acid medium to form molybdenum blue. The molybdenum blue colour is measured in a colourimeter at 660-mu wavelength.

3. Interferences

3.1. The only known interferences with the method are mercury and arsenic. Mercury at levels above 1 mg/l Hg gives a precipitate of mercurous chloride and mercury in the reduction step. This is not a problem with natural waters unless mercuric chloride has been used to "preserve" the sample. If it is suspected that arsenic is in a sample, its concentration must be measured and a correction made on the "phosphate" value obtained by this method. The amount of correction can be determined by running a blank containing the same arsenic concentration found in the sample following the phosphate procedure and subtracting the "apparent" phosphate level obtained from the "phosphate" level obtained on the sample.

3.2. At the concentration of sulphuric acid used in the method, silica does not interfere.

4. Sampling Procedure and Storage

4.1. The sample should be cooled to about 4°C as soon as it has been taken. Analysis should be carried out on the same day.

5. Sample Preparation

5.1. If dissolved inorganic phosphate is to be determined, the sample aliquot used for the analysis should be free from turbidity or filtered through a 0.45-micron membrane filter.

5.2. If total inorganic phosphate is to be determined, the sample should be well mixed before the aliquot is taken for analysis.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler.

6.1.2. Heating bath, 30°C.

6.1.3. Manifold.

6.1.4. Proportioning pump.

6.1.5. Colorimeters (2), one with a 50-mm flow cell and one with a 15-mm flow cell; two sets of 660-mu filters.

6.1.6. Recorder, two-pen.

6.1.7. Range expander.

6.2. A "Castle" No. 999 - C electrically heated autoclave or equivalent.

7. Reagents

7.1. Ammonium molybdate solution: Dissolve 25 g ammonium molybdate, $(NH_4)_6MO_7O_{24}.4H_2O$, in 175 ml distilled water; to 400 ml distilled water add 280 ml conc H_2SO_4; add the molybdate solution to the acid solution and dilute to 1 litre.

7.2. Stock stannous chloride solution: Dissolve 5 g stannous chloride, $SnCl_2.2H_2O$, in 25 ml conc HCl, dilute to 500 ml with distilled water; this stock is stable for two weeks at 5°C storage.

7.3. Stannous chloride working solution: To 30-ml stock solution (7.2), add 25 ml conc HCl and dilute to 500 ml with distilled water; this solution is stable for 12 hours and generally is sufficient for one day.

7.4. Strong acid solution: To 600 ml distilled water add 300 ml conc H_2SO_4. Cool, add 4 ml conc HNO_3 and dilute to one litre.

7.5. Standard phosphate solutions: See orthophosphate method (7.4 - 7.7) for preparation.

7.6. "Blank" reagents: prepare "blank" ammonium molybdate and stannous chloride reagents as in 7.1 and 7.2 above but do not add the ammonium molybdate and stannous chloride respectively.

8. Procedure

8.1. Add 50 ml of the standard solutions each to 100-ml beakers; to each beaker add 0.5 ml strong acid solution (7.4).

8.2. Add 50 ml of water samples to each 100-ml beaker; to each beaker add 0.5 ml of strong acid solution (7.4).

8.3. Autoclave the beakers by the following procedure:

8.3.1. Place beakers in the autoclave. Turn handle to "autoclave" position.

8.3.2. When chamber pressure reaches 15 psig. (250°F), time the digestion for 30 minutes.

8.3.3. After digestion, turn the handle to "liquids cool" position and allow chamber pressure to drop to zero.

8.3.4. Turn handle to "standby and vent" position.

8.3.5. Remove beakers and allow to cool.

8.4. If there is any turbidity present after the autoclaving, filter the solutions through a 0.45-micron membrane filter.

8.5. Run the standards and samples after autoclaving at 20 samples per hour using the manifold as shown in Figure 14. The colourimeter with the 50-mm flow cell is used to measure concentrations in the range 5 to 50 ug/l, the colourimeter with the 15-mm flow cell is used to measure concentrations in the 50 to 200 ug/l range.

8.6. Every time a new batch of stannous chloride reagent is used a set of standard solutions must be run. Standard solutions should be run periodically to check the validity of the calibration curve.

8.7. If any of the samples after autoclaving and filtering contain a significant level of colour, a correction should be made by re-running these samples through the system with the "blank" reagents (7.6). (A decision as to what constitutes a significant level of colour can only be made on experience gained by re-running samples of 'doubtful' levels of colour).

9. Calculation

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of inorganic phosphate in the samples by comparing sample peak heights with the calibration curve.

9.3. If a sample has been re-run with "blank" reagents, the inorganic phosphate level in the original sample is determined by subtracting the "apparent" phosphate level obtained with the blank reagents from the "phosphate" level obtained with the sample and "regular" reagents.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at phosphate levels of 20 and 50 ug/l PO_4 were ±9.98% and ±4.71% respectively.

11. Reference

11.1. Unpublished information. Method developed in Water Quality Division, Ottawa.

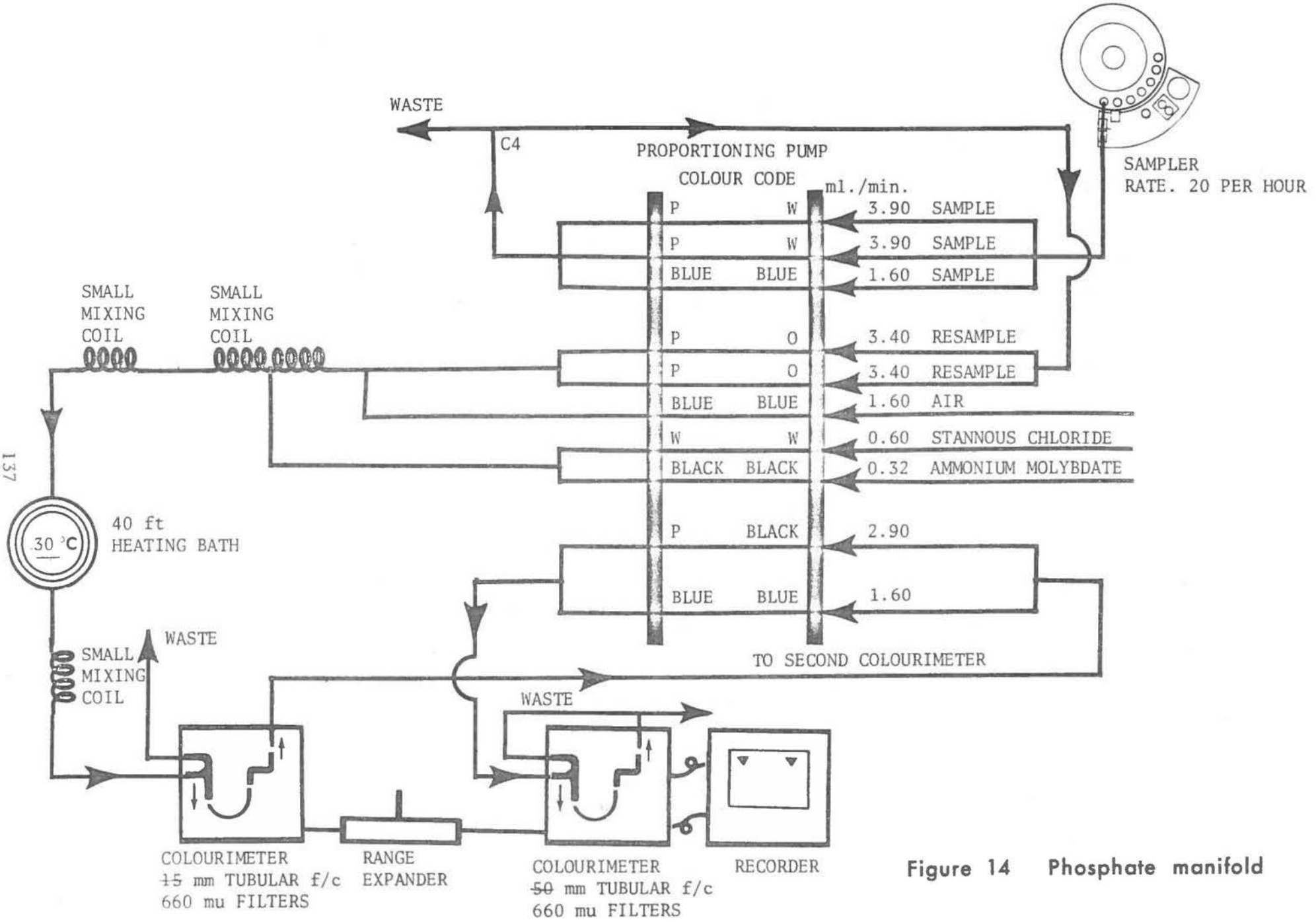

Figure 14 Phosphate manifold

PHOSPHATE, ORTHO

1. Scope and Application

1.1. This colourimetric method is applicable to surface and ground waters with orthophosphate levels in the range 5 to 200 ug/l (PO_4). Samples having higher concentrations than this can be measured by appropriate dilution of an aliquot.

2. Principle of Method

2.1. The orthophosphate in a sample is reacted with ammonium molybdate to form the heteropoly molybdophosphoric acid. This is then reduced with stannous chloride in aqueous sulphuric acid medium to form molybdenum blue. The molybdenum blue colour is measured in a colourimeter at 660-mu wavelength.

3. Interferences

3.1. The only known interferences with the method are mercury and arsenic. Mercury at levels above 1 mg/l Hg gives a precipitate of mercurous chloride and mercury in the reduction step. This is not a problem with natural waters unless mercuric chloride has been used to "preserve" the sample. If it is suspected that arsenic is in a sample, its concentration must be measured and a correction made on the "phosphate" value obtained by this method. The amount of correction can be determined by running a blank containing the same arsenic concentration found in the sample following the phosphate procedure and subtracting the "apparent" phosphate level obtained from the "phosphate" level obtained on the sample.

3.2. At the concentration of sulphuric acid used in the method, silica does not interfere.

4. Sampling Procedure and Storage

4.1. The sample should be cooled to about 4°C as soon as it has been taken. Analysis should be carried out the same day.

5. Sample Preparation

5.1. The sample aliquot used for the analysis should either be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler.

6.1.2. Heating bath, 30°C.

6.1.3. Manifold.

6.1.4. Proportioning pump.

6.1.5. Colourimeters (2), one with a 50-mm flow cell and one with a 15-mm flow cell; two sets of 660-mu filters.

6.1.6. Recorder, two-pen.

6.1.7. Range expander.

7. Reagents

7.1. Ammonium molybdate solution: Dissolve 25 g ammonium molybdate, $(NH_4)_6MO_7O_{24}.4H_2O$, in 175 ml distilled water; to 400 ml distilled water add 280 ml conc H_2SO_4, add the molybdate solution to the acid solution and dilute to 1 litre.

7.2. Stock stannous chloride solution: Dissolve 5 g stannous chloride, $SnCl_2.2H_2O$, in 25 ml conc HCl, dilute to 500 ml with distilled water; this stock solution is stable for two weeks at 5°C storage.

7.3. Stannous chloride working solution: To 30 ml stock solution (7.2) add 25 ml conc HCl and dilute to 500 ml with distilled water; this solution is stable for 12 hours and generally is sufficient for one day.

7.4. Stock phosphate solution 200 mg/l PO_4: Dissolve 0.2866 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, (oven dried at 105°C) in distilled water and dilute to 1 litre. Store in amber or dark coloured bottle.

7.5. Intermediate phosphate solution 10 mg/l PO_4: Pipette 50 ml stock solution (7.4) into a 1-litre volumetric flask and dilute to the mark.

7.6. Standard phosphate solution 1000 ug/l PO_4: Pipette 50 ml intermediate solution (7.5) into a 500-ml volumetric flask and dilute to the mark; prepare daily.

7.7. Working phosphate solutions: Using the standard solution (7.6), prepare the following working solutions in 100-ml volumetric flasks:

ml of Standard Solution (1000 ug/l PO_4)	Concentration, ug/l
0	0
0.5	5
1.0	10
3.0	30
5.0	50
8.0	80
10.0	100
15.0	150
20.0	200

7.8. "Blank" reagents: Prepare "blank" ammonium molybdate and "blank" stannous chloride reagents as in 7.1 and 7.2 above but do not add the ammonium molybdate and stannous chloride respectively.

8. Procedure

8.1. Run the standards and samples at 20 per hour using the manifold as shown in Figure 14 (See Phosphate, Inorganic). The colourimeter with the 50-mm flow cell is used to measure concentrations in the range 5 to 50 ug/l; the colourimeter with the 15-mm flow cell is used to measure concentrations in the 50 to 200 ug/l range.

8.2. Every time a new batch of stannous chloride reagent is used, a set of standard solutions must be run. Standard solutions should be run periodically to check the validity of the calibration curve.

8.3. If any samples contain a significant level of colour, a correction should be made by re-running these samples through the system with the blank reagents (7.8). (A decision as to what constitutes a significant level of colour can only be made on experience gained by re-running samples of 'doubtful' levels of colour).

9. Calculation

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of orthophosphate in the samples by comparing sample peak heights with the calibration curve.

9.3. If a sample has been re-run with "blank" reagents, the orthophosphate level in the original sample is determined by subtracting the "apparent" orthophosphate level obtained with the blank reagents from the "orthophosphate" level obtained with the sample and regular reagents.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at orthophosphate levels of 10 and 25 ug/l PO_4 were ±4.65% and ±3.98%, respectively.

11. Reference

11.1. Unpublished information. Method developed in Water Quality Division, Ottawa.

PHOSPHORUS, TOTAL

1. Scope and Application

1.1. This colourimetric method is applicable to surface and ground waters with total phosphorus levels in the range 5 to 200 ug/l (PO_4). Samples having higher concentrations can be measured by appropriate dilution of an aliquot.

2. Principle of the Method

2.1. The organic material in a sample is destroyed by digestion with a sulphuric acid - persulphate mixture. This releases the organically bound phosphorus as phosphate. The digestion with acid also hydrolyzes polyphosphates to orthophosphate. This orthophosphate is then reacted with ammonium molybdate to form heteropoly molybdophosphoric acid. This is reduced with stannous chloride in an aqueous sulphuric acid medium to form molybdenum blue. The molybdenum blue colour is measured in a colourimeter at 660-mu wavelength.

3. Interferences

3.1. The only known interferences with the method are mercury and arsenic. Mercury at levels above 1 mg/l Hg gives a precipitate of mercurous chloride and mercury in the reduction step. This is not a problem with natural waters unless mercuric chloride has been used to 'preserve' the samples. If it is suspected that arsenic is in a sample its concentration must be measured and a correction made on the "phosphate" value obtained by this method. The amount of correction can be determined by running a blank containing the same arsenic concentration found in the sample following the phosphate procedure and subtracting the "apparent" phosphate level obtained from the "phosphate" level obtained on the sample.

3.2. At the concentration of sulphuric acid used in the method, silica does not interfere.

4. Sampling Procedure and Storage

4.1. No special precautions are necessary in the sampling or storage of the sample. However, if the analysis cannot be carried out within one week of the sample being taken, the sample should be well shaken and 50 ml transferred to a 125-ml Erlenmeyer flask fitted with a ground-glass stopper. This stoppered flask may be stored for months. The digestion, as described in section 8, is carried out on the total contents of this flask.

5. Sample Preparation

5.1. The sample should be well mixed before the aliquot is taken for analysis.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler.

6.1.2. Heating bath, 30°C.

6.1.3. Manifold.

6.1.4. Proportioning pump.

6.1.5. Colourimeters (2), one with a 50-mm flow cell and one with a 15-mm flow cell; two sets of 660-mu filters.

6.1.6. Recorder, two-pen.

6.1.7. Range expander.

6.2. A "CASTLE" No. 999-C electrically heated autoclave or equivalent.

7. Reagents

7.1. Ammonium molybdate solution: dissolve 25 g ammonium molybdate, $(NH_4)_6MO_7O_{24}.4H_2O$, in 175 ml distilled water. To 400 ml distilled water add 280 ml conc H_2SO_4. Add the molybdate solution to the acid solution and dilute to 1 litre.

7.2. Stock stannous chloride solution: Dissolve 5 g stannous chloride, $SnCl_2.2H_2O$, in 25 ml conc HCl, dilute to 500 ml with distilled water; this stock is stable for two weeks at 5°C storage.

7.3. Stannous chloride working solution: To 30 ml stock add 25 ml conc HCl and dilute to 500 ml with distilled water; this solution is stable for 12 hours and generally is sufficient for one day.

7.4. Strong acid solution: To 600 ml distilled water add 300 ml of conc H_2SO_4. Cool; add 4 ml of conc HNO_3 and dilute to one litre.

7.5. Standard phosphate solutions: See orthophosphate method (7.4 - 7.7) for preparation.

7.6. "Blank" reagents: Prepare "blank" ammonium molybdate and stannous chloride reagents as in 7.1 and 7.2 above but do not add the ammonium molybdate and stannous chloride respectively.

7.7. Potassium persulphate: Solid form ACS grade.

8. Procedure

8.1. Add 50 ml standard solutions each to a 100-ml beaker. Add 0.5 ml strong acid solution (7.4). Add 0.2 g potassium persulphate. (N.B. It is acceptable to add the potassium persulphate by a volumetric measure once such a measure has been calibrated).

8.2. Add 50 ml of each water sample to a 100-ml beaker; treat as in 8.1 above.

8.3. If the samples have been stored in 125-ml Erlenmeyer flasks, (section 4) add the strong acid and potassium persulphate directly to these flasks.

8.4. Autoclave the beakers (or flasks) by the following procedure:

8.4.1. Place beakers in the autoclave. Turn handle to "autoclave" position.

8.4.2. When chamber pressure reaches 15 psig. (250°F), time the digestion for 30 minutes.

8.4.3. After digestion, turn the handle to "liquids cool" position and allow chamber pressure to drop to zero.

8.4.4. Turn handle to "standby and vent" position.

8.4.5. Remove beakers and allow to cool.

8.5. If there is any turbidity present after autoclaving, filter the solutions through a 0.45-micron membrane filter.

8.6. Run the standards and samples after autoclaving at 20 samples per hour using the manifold as shown in Figure 14 (see Phosphate, Inorganic). The colourimeter with the 50-mm flow cell is used to measure concentrations in the range 5 to 50 ug/l; the colourimeter with the 15-mm flow cell is used to measure concentrations in the 50 to 200 ug/l range.

8.7. Every time a new batch of stannous chloride reagent is used, a set of standard solutions must be run. Standard solutions should be run periodically to check the validity of the calibration curve.

8.8. If any of the samples after autoclaving and filtering contain a significant level of colour, a correction should be made by re-running these samples through the AutoAnalyzer with the "blank" reagents (7.6). (A decision as to what constitutes a significant level of colour can only be made on experience gained by re-running samples of doubtful levels of colour).

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentrations of phosphorus in the samples by comparing sample peak heights with the calibration curve.

9.3. If a sample has been re-run with "blank" reagents, the phosphorus level in the original sample is determined by subtracting the "apparent" phosphorus level obtained with the blank reagents from the "phosphorus" level obtained with the sample and regular reagents.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at phosphate levels of 20 and 50 ug/l PO_4 were ±7.30% and ±4.11% respectively.

11. Reference

11.1. Unpublished information. Method developed in Water Quality Division, Ottawa.

RESIDUE

1. Scope and Application

1.1. These methods are applicable to surface, ground, and waste waters in the range 10 to 30,000 mg/1.

2. Principle of Method

2.1. Definitions.

2.1.1. Residue, filterable: The residue remaining in a weighed dish after passing a sample through a standard glass fiber filter and dried to constant weight at 105°C.

2.1.2. Residue, nonfilterable: The residue retained by a glass fiber filter and dried to constant weight at 105°C.

2.1.3. Residue, fixed filterable: The residue remaining when the dish with the residue retained after completion of the test for filterable residue is subjected to heat for 1 hr in a furnace held at 550°C.

2.1.4. Residue, fixed nonfilterable: The residue remaining when the filter with its residue retained after the completion of the test for nonfilterable residue, are subjected to heat for 1 hr in a furnace held at 550°C.

3. Interferences

3.1. Large floating particles or submerged agglomerates (i.e., non-homogeneous materials) should be excluded from the test sample.

3.2. Floating oil and grease, if present, should be included in the sample and dispersed by a high-speed blender before taking aliquots.

3.3. If too much residue is present on the dish, then water is entrained and the drying time will be much longer.

4. Sampling Procedure and Storage

4.1. Equilibrium conditions may change sufficiently to alter the suspended fraction of materials in a water sample. Hence, the measurements should be made as rapidly as possible after the sample collection.

5. Sample Preparation

5.1. Residue, filterable: Sample is filtered through a glass fibre filter.

5.2. Residue, nonfilterable: Sample is thoroughly shaken prior to sampling for test.

5.3. The precautions listed in (3) above should be observed.

6. Apparatus

6.1. Whatman GF/C glass fibre filter of 4.25-cm diameter.

6.2. Millipore vacuum filtration equipment, aspirator, forceps, etc.

6.3. Porcelain dishes of 100-ml capacity and 90-mm diameter.

6.4. Oven set to 105°C.

6.5. Boiling water (steam) bath.

6.6. Muffle furnace set to 550°C.

6.7. Platinum dishes of about 100-ml capacity.

6.8. Platinum - tipped tongs to handle platinum ware.

6.9. Desiccator.

6.10. Analytical balance of 200-g capacity, weighing to 0.1 mg.

7. Reagents

7.1. No special reagents required

8. Procedure

8.1. Residue, nonfilterable.

8.1.1. Using forceps, transfer a washed glass fibre Whatman GF/C filter of 4.25-cm diameter to a porcelain dish; ignite in a furnace at 550°C for 15 min; cool in a desiccator, remove the filter and weigh.

8.1.2. The sample aliquot is measured out and filtered through the weighed filter on a Millipore filtration unit, using a vacuum aspirator. The flask and filter are rinsed three times with 10-ml portions of distilled water and the filtrate retained for the residue, filterable and residue, fixed filterable tests.

8.1.3. The wet filter is transferred to the porcelain dish and oven-dried at 105°C for 2½ hours, then cooled for 15 min in a desiccator containing calcium chloride, and the filter weighed. This gives the weight of the filter mat and the nonfilterable residue. The increase in weight over that of the empty filter represents the nonfilterable residue.

8.2. Residue, fixed nonfilterable.

8.2.1. The porcelain dish and filter are now placed in a muffle furnace set at 550°C for 30 min, cooled in a desiccator and the filter re-weighed. The increase in weight over that of the empty filter represents residue, fixed nonfilterable.

8.3. Residue, filterable.

8.3.1. The filtrate from procedure 8.1.2. above is used, or if the residue, nonfilterable is not determined, then at least 250 ml of the sample is filtered through a glass-fibre filter and the filtrate retained for the test.

8.3.2. A clean platinum dish is ignited at 550°C in the muffle furnace for 30 min, transferred with platinum tipped tongs to a desiccator for cooling, and weighed after 15 min.

8.3.3. The filtrate aliquot is evaporated to dryness in the dish on a steam bath (boiling water).

8.3.4. The dish and its residue are oven-dried over night at 105°C and weighed to a constant value after cooling for 15 min in a desiccator. The increase in weight over that of the empty dish represents residue, filterable.

8.4. Residue, fixed filterable.

8.4.1. The platinum dish and contents are ignited in the muffle furnace for $2\frac{1}{2}$ hours at 550°C, cooled in a desiccator for 15 min and re-weighed. The increase in weight over that of the empty dish represents residue, fixed filterable.

NOTE: All weights expressed in mg.

9. Calculations

9.1. Residue, nonfilterable is calculated after drying and weighing the filter with its residue at 105°C, as follows:

Residue, nonfilterable, mg/l =

$$\frac{(\text{wt of dried filter + residue - wt of filter}) \times 1000}{\text{ml sample}}$$

9.2. Residue, fixed nonfilterable is calculated after ignition at 550°C of the sample retained after completion of the test for residue, nonfilterable, as follows:

Residue, fixed nonfilterable, mg/l =

$$\frac{(\text{wt of ignited filter + residue - wt of filter}) \times 1000}{\text{ml sample}}$$

9.3. Residue, filterable is calculated after drying the platinum dish with its residue at 105°C, as follows:

Residue, filterable, mg/l =

$$\frac{(\text{wt of dried residue + dish - wt of dish}) \times 1000}{\text{ml sample}}$$

9.4. Residue, fixed filterable is calculated after ignition at 550°C of the sample retained after completion of the test for residue, filterable, as follows:

Residue, fixed filterable, mg/l =

$$\frac{(\text{wt of ignited residue + dish - wt of dish}) \times 1000}{\text{ml sample}}$$

10. Precision and Accuracy

10.1. No data available.

11. References

11.1. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

11.2. Federal Water Pollution Control Administration, 1969. FWPCA Methods for Chemical Analysis of Water and Wastes, U.S. Department of the Interior, Cincinnati, Ohio.

11.3. Melbourne, K.V. 1964. Determination of suspended solids in sewage and related suspensions. The Journal and Proceedings of the Institute of Sewage Purification, Part 4.

SILICA, REACTIVE

(Automated Heteropoly Blue Method)

1. Scope and Application

1.1. This automated method is applicable to the determination of silica in surface, ground, and sea waters. The applicable range is 0.5 to 20 mg/l SiO_2; however, the range can be extended down to 0.005 mg/l by slight modification, and upward by dilution of the original sample.

2. Principle of Method

2.1. Ammonium molybdate at approximately pH 1.2 reacts with silica and also with any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid but not the molybdosilicic acid. The yellow colour produced is reduced by means of aminonaphtholsulphonic acid to heteropoly blue. The blue colour is more intense than the yellow colour and is proportional to the "molybdate-reactive" silica. The colour is measured in a colourimeter at 660 mu.

3. Interferences

3.1. There are no significant interferences.

4. Sampling Procedure and Storage

4.1. Sample should be collected in a polyethylene bottle. Glass containers should not be used.

4.2. For low level silica analysis such as found in waters of the Great Lakes, the test should be carried out within 8 hours after collection.

5. Sample Preparation

5.1. The sample aliquot either should be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler.

6.1.2. Manifold.

6.1.3. Proportioning pump.

6.1.4. Colourimeter, equipped with a 50-mm flow cell and 660-mu filters.

6.1.5. Recorder.

6.1.6. Range expander.

7. Reagents

7.1. Stock silica solution, 1000 mg/l SiO_2: Dissolve 4.73 g reagent grade sodium metasilicate, $Na_2SiO_3.9H_2O$, in distilled water and dilute to 1 litre. This solution should be checked using the Standard Method (11.2) gravimetric procedure. Adjust the remainder of the solution to contain exactly 1000 mg/l SiO_2. Alternately, an accurate stock silica solution may be purchased from Hartman-Leddon Co. (Canlab).

7.2. Standard silica solutions: Prepare a series of standard silica solutions by diluting suitable aliquots of stock silica solution (7.1) to 1 litre with distilled water.

7.3. Ammonium molybdate solution: Dissolve 40 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 400 ml distilled water and dilute to 2 litres. Filter.

7.4. Sulphuric acid solution, 0.2N: To 500 ml distilled water add 11.1 ml conc sulphuric acid and dilute to 2 litres.

7.5. Oxalic acid solution: Dissolve 100 g oxalic acid, $H_2C_2O_4.2H_2O$, in 800 ml distilled water and dilute to 2 litres.

7.6. Stock ANSA solution: Dissolve in distilled water 150 g sodium bisulphate, $NaHSO_3$; 5 g anhydrous sodium sulphite, Na_2SO_3; and 2.5 g 1-amino-2-naphthol-4-sulphonic acid (ANSA) and dilute to 1250 ml.

7.7. Working ANSA solution: Dilute 200 ml stock ANSA solution (7.6) to 2 litres with distilled water.

7.8. Synthetic sea water: Dissolve 25 g sodium chloride, NaCl, and 8 g magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, in distilled water and dilute to 1 litre.

8. Procedure

8.1. If sea water samples are to be determined, it is necessary to run the base line using synthetic sea water solution instead of distilled water. Also, the standard silica solutions must be made up using the synthetic sea water solution as dilution water.

8.2. Run the samples and standards at 20 per hour using the manifold as shown in Figure 15.

8.3. If lower limits of detection are required, replace the dilution line (See Manifold) for a sample line and install a range expander (X10) in the system. With these changes, it is possible to accurately determine as low as 5 ug/l SiO_2.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of silica in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at the 200 ug/l SiO_2 level was ±0.7%.

11. References

11.1. Technicon Instruments Corp. 1969. AutoAnalyser Methodology 111F.

11.2. American Public Health Association, 1965. Standard methods for the examination of water and wastewater. Twelfth Ed., New York.

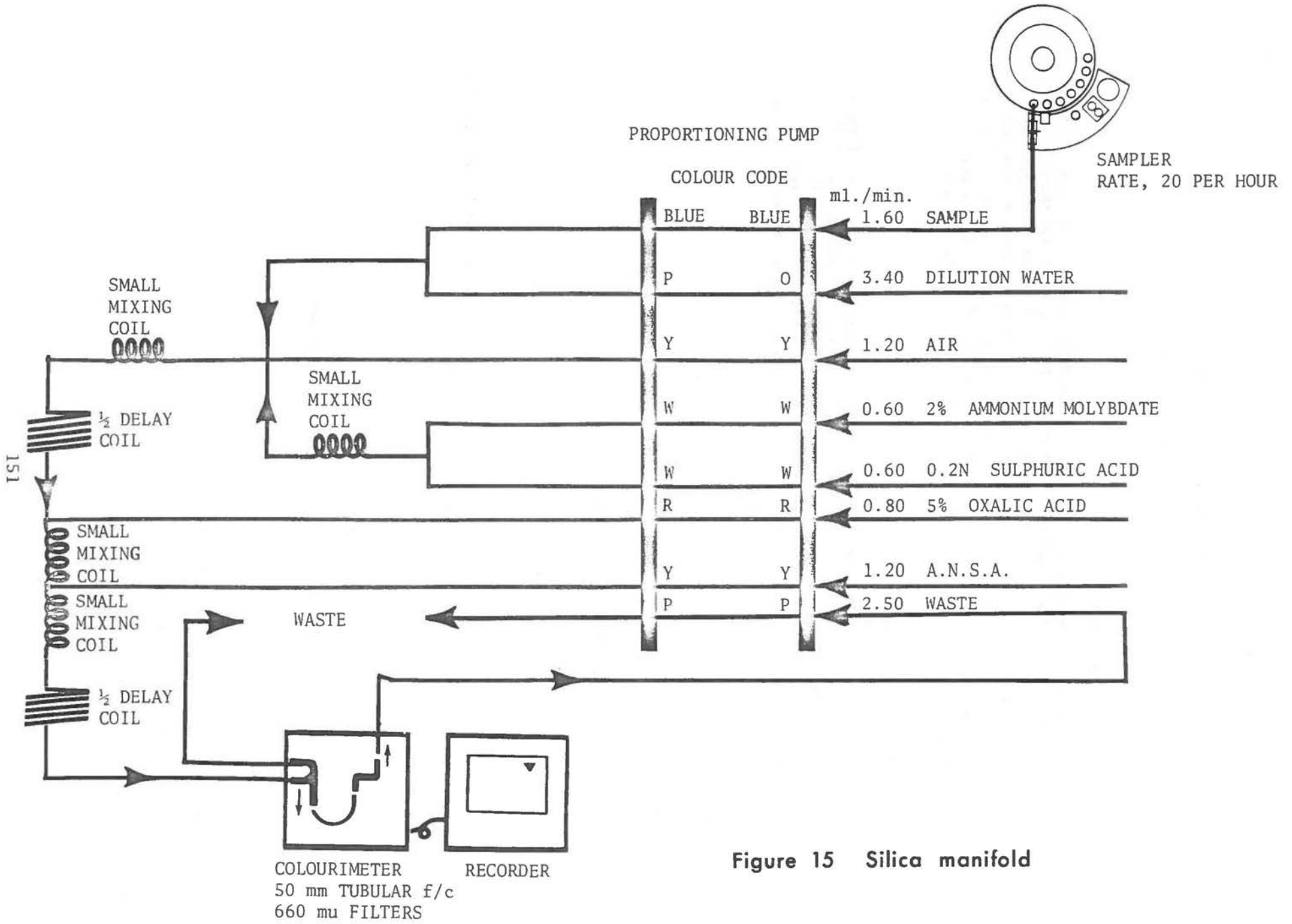

Figure 15 Silica manifold

SODIUM AND POTASSIUM

(Automated Flame Photometric Method)

1. Scope and Application

1.1. Sodium and Potassium are determined simultaneously on the same sample using a two-channel module flame photometer or, on a one-channel module, are run separately. This method can be applied to surface, ground and saline waters and all ranges of concentration can be determined. The ranges most commonly used are 0-100 mg/l for sodium and 0-30 mg/l for potassium. Higher concentrations may be measured by slight modification to the method or by dilution of a sample aliquot.

2. Principle of Method

2.1. In this automated procedure, the sample is mixed with lithium nitrate as an internal standard, dialyzed, and passed into the burner of the flame photometer equipped with interference filters to isolate the spectral lines of sodium and potassium. The intensity of light produced by both sodium and potassium is proportional to each element and is charted on a recorder.

3. Interferences

3.1. There are no serious interferences.

4. Sampling Procedure and Storage

4.1. No special precautions.

5. Sample Preparation

5.1. As each sample is automatically dialyzed, only samples with considerable turbidity need be filtered before analyses.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Flame photometer module, single or dual-channel.

6.1.2. Sampler.

6.1.3. Dialyzer.

6.1.4. Manifold for sodium and/or potassium.

6.1.5. Proportioning pump.

6.1.6. Recorder.

7. Reagents

7.1. Lithium nitrate stock, 10,000 mg/l Li: Dissolve 99.35 g lithium nitrate, $LiNO_3$, in distilled water and dilute to 1 litre.

7.2. Lithium nitrate working solution, 1,000 mg/l Li: Dilute 100 ml lithium nitrate stock (7.1) to 1 litre with distilled water.

7.3. Sodium stock solution, 1000 mg/l Na: Dissolve 2.5420 g sodium chloride, NaCl, in distilled water and dilute to 1 litre.

7.4. Potassium stock solution, 1000 mg/l K: Dissolve 1.9066 g potassium chloride, KCl, in distilled water and dilute to 1 litre.

7.5. Sodium and potassium working solutions: Dilute sodium and potassium stock solutions as required.

8. Procedure

8.1. The analyst should follow the Technicon instruction manual supplied with his particular instrument. As a rule, the following steps are followed:

8.1.1. Open both oxygen and natural gas main tank valves to maximum. Slowly open natural gas valve on module and apply lighted match to burner tip. A yellow flame will appear. Slowly turn this gas valve until flame reaches chimney height.

8.1.2. Open oxygen pilot valve and small blue flames will appear on the tips of the three pilot tubes. Continue oxygen input until one or more of the three blue flames rise off the pilot tubes. At this point, slowly close oxygen valve until the three blue flames return to the pilot tubes. Turn counter-clockwise main oxygen valve on module until flame turns blue and its inner cone reaches a height of about 3/4 inch. Allow about $\frac{1}{2}$-hour warm-up period.

8.1.3. Run samples and standards at 20 per hr using the manifold shown in Figure 16.

8.1.4. After completion of samples and standards, wash out the system with distilled water for 15 min.

8.1.5. Shut off pump and allow 5 min for burner to expel liquids.

8.1.6. Shut off oxygen and then the gas.

8.2. If only a small number of samples have higher concentrations of sodium and/or potassium than the highest standard, dilute the samples and re-run using the same manifold.

8.3. If many samples have high sodium and/or potassium concentrations, dilute the samples with distilled water using the pump and re-cycle the diluted samples to the original manifold assembly. Higher concentrations of sodium and potassium standards should also be prepared.

9. Calculations

9.1. Prepare calibration curves derived from the peak heights obtained with the sodium and potassium standards.

9.2. Determine the concentration of sodium and potassium in the samples by comparing sample peak heights with the calibration curves.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at sodium levels of 12 mg/l and 67 mg/l Na were ±0.67% and ±1.29% respectively.

10.2. In a single laboratory (Water Quality Division), the coefficients of variation at potassium levels of 6.4 mg/l and 36 mg/l K were ±1.09% and ±1.79% respectively.

11. Reference

11.1. Technicon AutoAnalyzer Methodology N-20b.

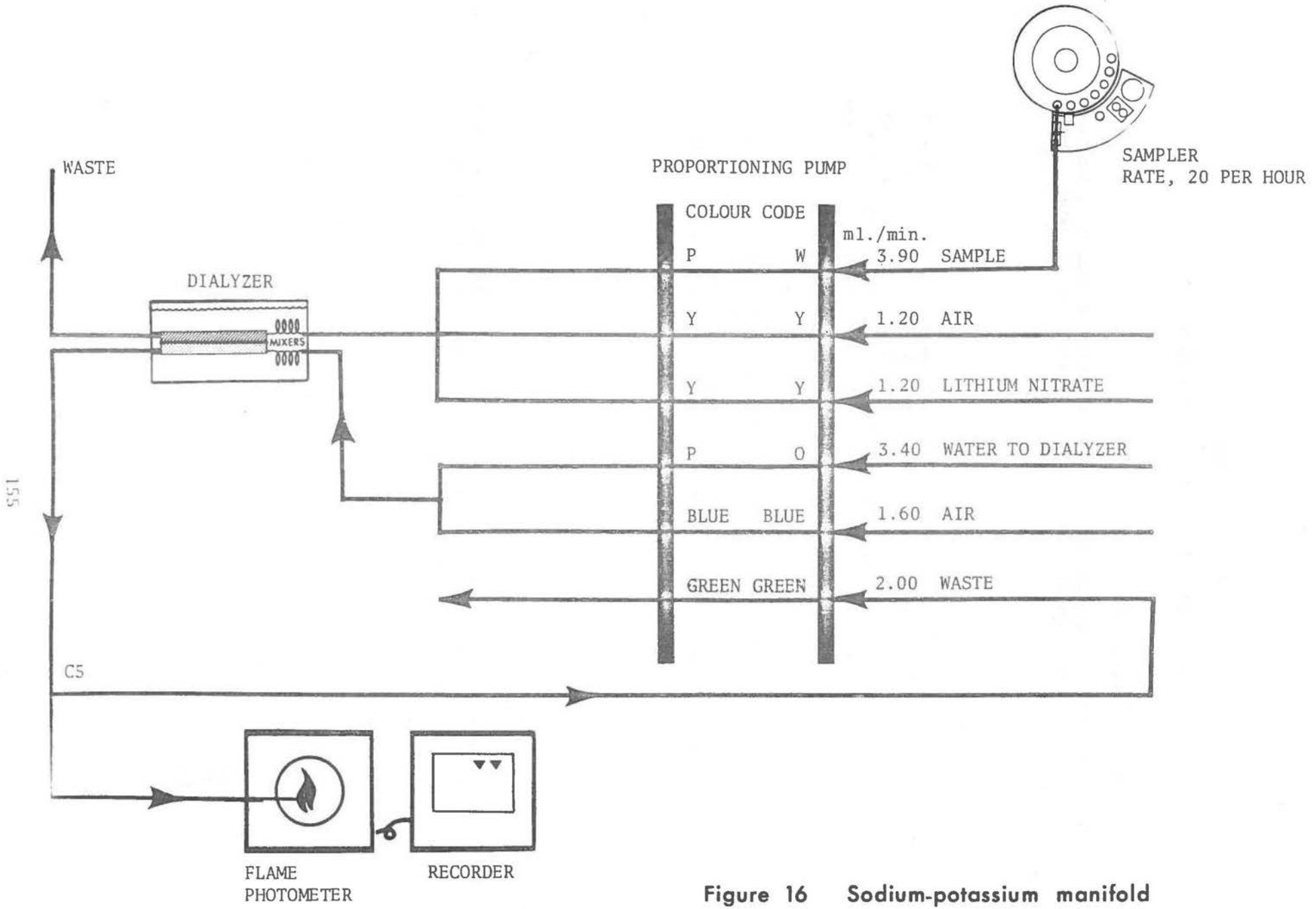

Figure 16 Sodium-potassium manifold

SPECIFIC CONDUCTANCE

(Radiometer Type CDM2 Conductivity Meter)

1. Scope and Application

1.1. This method is applicable to the determination of specific conductance in surface and ground waters, industrial wastes and sea water. The lower limit is about 0.2 micromhos/cm; higher ranges can be measured directly.

2. Principle of Method

2.1. The "conductivity" of a solution refers to ability of the solution to carry an electric current. Since electricity is carried in the solution by migration of the solute ions, the conductivity bears some relationship to the total ionic concentration of the solution. The principle of the conductivity meter is that of an ohmeter in which the resistance is measured in ohms. The standard unit of electrical conductivity is the reciprocal of the resistance in ohms and is written in terms of micromhos/cm or μmhos/cm, usually at 25°C. Using the instrument described in this method, the conductivity of the test solution is read directly from the indicating meter, and the specific conductance of the test solution at the temperature of the solution is had by correcting the conductivity read with a correction which is engraved on the cell; the specific conductance is then corrected to 25°C.

3. Interferences

3.1. There are no serious interferences.

4. Sampling Procedure and Storage

4.1. The plastic sample container should be tightly sealed immediately after collection of the sample and the specific conductance determined as soon as the bottle is opened.

5. Sample Preparation

5.1. Sample should be allowed to reach laboratory temperature before measurement of specific conductance. A sample aliquot should be decanted into a beaker for the test or the conductivity cell dipped directly into the sample container.

6. Apparatus

6.1. Radiometer Type CDM2 Conductivity Meter or equivalent.

6.2. Conductivity cell, Radiometer type CDC104 or CDC114.

7. Reagents

7.1. Standard potassium chloride, 0.010M: Dissolve 0.7456 g anhydrous potassium chloride, KCl, in distilled water and make up to 1 litre at 25°C. This is a standard reference solution which, at 25°C, has a specific conductance of 1,413 micromhos/cm.

8. Procedure

8.1. Types of cells.

8.1.1. Type CDC104 Conductivity cell. This cell has 3 electrodes in the form of platinum sheets placed in rings around a glass tube and enclosed in a glass jacket. When using this cell, all three rings must be covered with the sample, and there must not be any air bubbles in the cell.

8.1.2. Type CDC114 Conductivity cell. This cell can be used as a pipette or a flow-through cell. It has 3 electrodes, the same as the type CDC104 cell. It uses a rubber bulb by means of which the cell can be filled. The same precautions stated for the type CDC104 cell apply to this cell.

8.2. Measurement of Samples

8.2.1. Switch on power and allow instrument to warm up for 5 min.

8.2.2. Mount and connect either of the two conductivity cells explained above.

8.2.3. Rinse the cell three times with the sample to be tested and then fill the cell with the sample.

8.2.4. Set the MEASURE-CALIBRATE switch to CALIBRATE and rotate the CALIBRATE knob until the needle rests at the triangular mark on the face of the meter.

8.2.5. Set the MEASURE-CALIBRATE switch to MEASURE and record the reading indicated by the indicator needle.

8.2.6. Record the temperature of the sample at the same time that the conductivity reading is being taken.

9. Calculation

9.1. Calculate the specific conductance of the sample as follows:

9.1.1. Cell CDC104:

Specific conductance = reading + correction percentage,

where specific conductance is in micromhos/cm at the temperature of the test, and the correction percentage is stated on the cell.

9.1.2. Cell CDC114:

$$\text{Specific conductance} = \frac{\text{reading}}{\text{correction number}}$$

where specific conductance is in micromhos/cm at the temperature of the test and the correction number is stated on the cell.

9.2. To obtain the specific conductance at 25°C, add 2% of the specific conductance value obtained at the test temperature for each °C temp. at test below 25°C or subtract 2% of the specific conductance value for each °C temp. at test above 25°C.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a level of 520 micromhos/cm was ±0.5%.

11. Reference

11.1. Radiometer Copenhagen. Direct reading conductivity meter, type CDM2, Denmark.

SUGAR

(Automated Phenol-Hydrazine Sulphate Method)

1. Scope and Application

1.1. This method can be used for the determination of sugars in the range 0 to 3 mg/l sugar expressed as D-xylose.

2. Principle of Method

2.1. The sugar is decomposed by heating with concentrated sulphuric acid and the addition of phenol and hydrazine sulphate gives a pink colouration whose intensity is proportional to the amount of sugar present and is measured at 490 mu using a 50-mm light path flow cell in the Technicon AutoAnalyzer.

3. Interferences

3.1. Unless removed by filtration, particulate carbohydrates, e.g., starches and cellulose fibres, etc., will be hydrolyzed to monosaccharides in varying extents by this method and so add to the soluble sugar value. Furan and its derivatives will behave similarly, if present, since this compound is an intermediate in the colour formation from sugars.

4. Sampling Procedure and Storage

4.1. The samples should be stored cold (4°C) to minimize sugar loss by bacterial decomposition.

5. Sample Preparation

5.1. The sample should either be free from turbidity or should be filtered through a 0.45-micron membrane filter.

6. Apparatus

6.1. Technicon AutoAnalyzer Unit consisting of:

6.1.1. Sampler with cam No. 127-B209 (1:5 ratio) giving 10 samples per hour.

6.1.2. Colourimeter, 50-mm path length flowcell, with 490-mu filter.

6.1.3. Proportioning pump.

6.1.4. Heating bath set at 100°C.

6.1.5. Recorder.

7. Reagents

7.1. Phenol stock solution: Dissolve 25 g phenol, C_6H_5OH, in distilled water and dilute to 1 litre. Fresh solutions are prepared daily and stored in amber bottles.

7.2. Hydrazine sulphate in concentrated sulphuric acid: A stock solution of 2.5 g/litre concentration is prepared by slowly adding hydrazine sulphate, $N_2H_4H_2SO_4$, to the acid, while stirring, at 40°C. After the solid has dissolved, the solution is rapidly cooled to room temperature by immersing the flask in ice-water in order to prevent possible decomposition of the salt. The daily preparation of fresh solutions is recommended.

7.3. Stock sugar solution, 10 mg/l D-xylose: Dissolve 10 mg in distilled water and dilute to 1 litre with distilled water. This solution is replaced daily because it is susceptible to bacterial decomposition.

7.4. Standard sugar solutions: From the stock sugar solution, prepare a series of standards by diluting suitable aliquots to 100 ml with distilled water.

8. Procedure

8.1. Run the samples and standards at 10 per hour using the manifold shown in Figure 17.

8.2. The following should be observed for successful operation:

8.2.1. Referring to the flowsheet diagram, all transmission tubing should be of acidflex, acid-resistant material to avoid plasticizer contamination.

8.2.2. All tubing in the manifold should be changed after 8 hours of operation.

8.2.3. Fresh D-xylose standard solutions should accompany the sample analysis frequently throughout the day's run to allow for instrument variations.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of sugar in the samples by comparing sample peak heights with the calibration curve.

9.3. The sugar concentrations in the samples are expressed as "D-xylose equivalent concentrations". Different saccharides develop a colour by this method at varying rates, hence giving different intensities at similar concentrations.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a concentration of 0.5 mg/l D-xylose was ±2.5%.

11. References

11.1. Regnier, Z. and A.E.P. Watson. 1970. An Automated Method for Sugar Estimation in Lake Waters. Methods and Properties Section, Water Quality Division, Inland Waters Branch, Ottawa.

11.2. Strickland J.D.H. and T.R. Parsons. 1968. A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Ottawa.

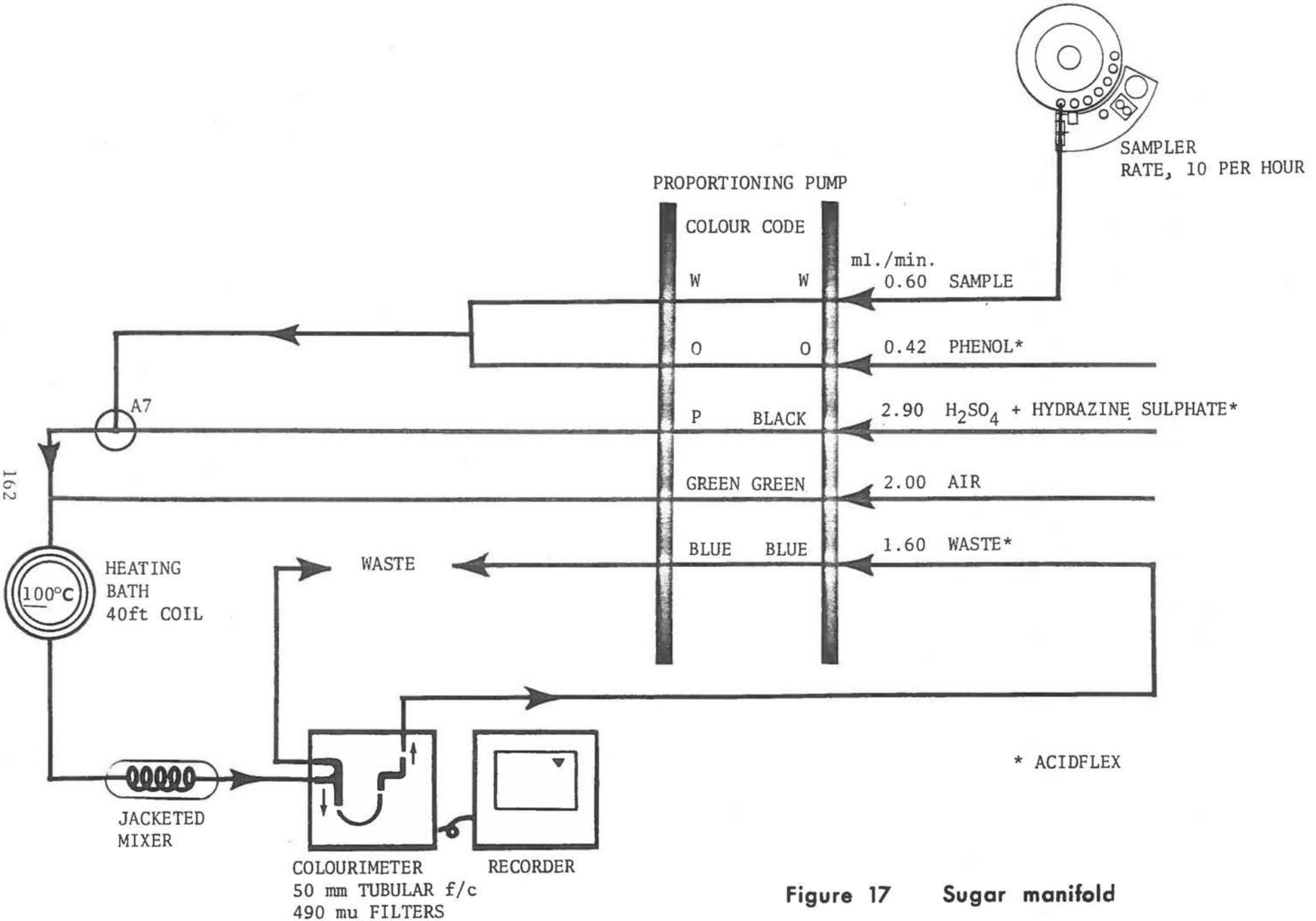

Figure 17 Sugar manifold

SULPHATE

(Titrimetric Method)

1. Scope and Application

1.1. This method is applicable to surface and ground waters in the range 5 to 150 mg/l SO_4. Samples having higher concentrations than this can be measured by appropriate dilution of an aliquot.

2. Principle of Method

2.1. Sulphate ion is titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution, using Thorin as the indicator.

3. Interferences

3.1. There are no interferences in normal waters; however, chloride ion in concentrations greater than 1000 mg/l cause an indistinct end point when the sulphate present is low (less than 10 mg/l). To overcome this interference, a known amount of sulphate can be added to an aliquot of the sample to increase the sulphate present.

4. Sampling Procedure and Storage

4.1. The sample container should be tightly capped as soon as the sample has been collected.

5. Sample Preparation

5.1. The sample aliquot used for analysis should either be free from turbidity or should be filtered through a 0.45-micron filter.

6. Apparatus

6.1. Titration assembly including a microburette, magnetic stirrer, stirring bars and titration lamp.

6.2. Casseroles, porcelain (100 to 125-ml capacity).

6.3. Ion exchange column: See Figure 18 for details. The exchange columns should be regenerated when about two thirds exhausted by passing the HCl (7.4) solution through the resin column and thoroughly washing with distilled water. The regeneration is generally carried out after two to three samples have passed through the column.

7. Reagents

7.1. Ethyl alcohol, C_2H_5OH: 95%.

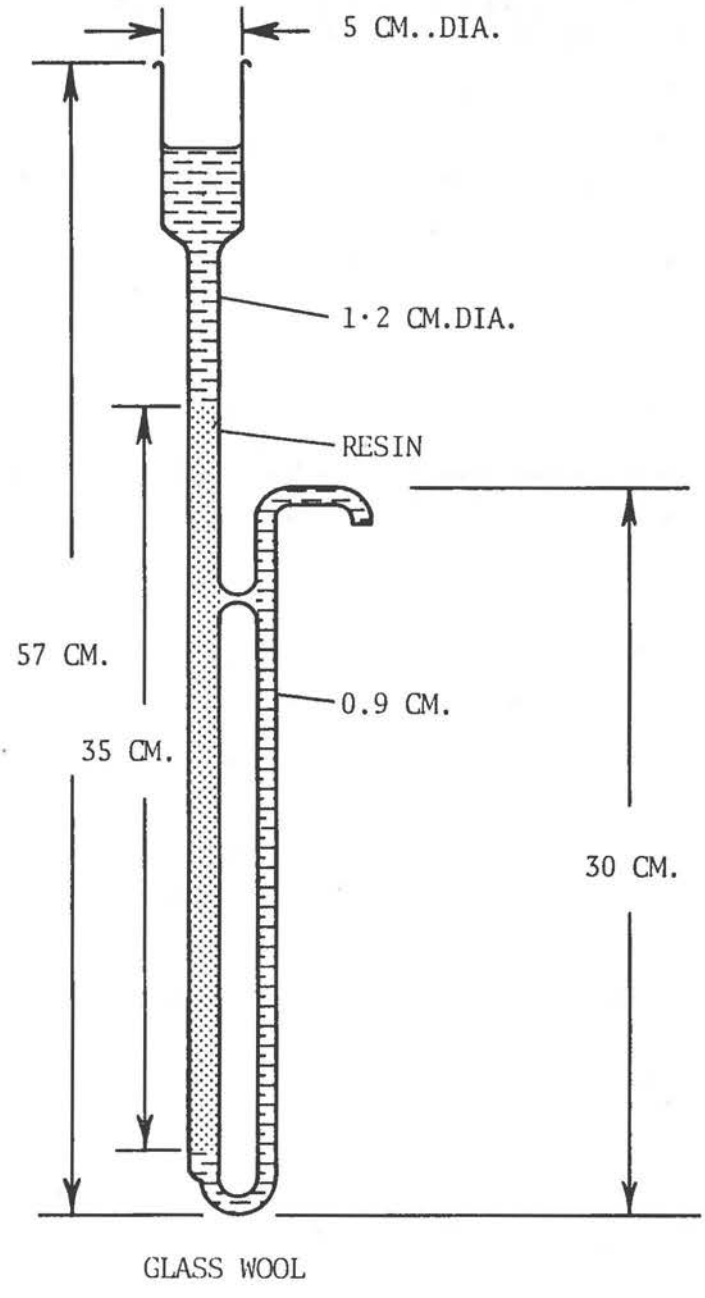

Figure 18 Ion-exchange column

7.2. Ammonium hydroxide solution: Mix one volume conc ammonium hydroxide, NH_4OH, with 99 volumes of distilled water.

7.3. Hydrochloric acid solution: Mix one volume conc hydrochloric acid, HCl, with 99 volumes of distilled water.

7.4. Hydrochloric acid solution (1 + 4): To each volume of conc hydrochloric acid, HCl, dilute with four volumes of distilled water.

7.5. Thorin solution: Dissolve 0.2 g Thorin [2(2-hydroxy -3,6-disulfo-1-naphtylazo) benzene arsonic acid], in 100 ml of distilled water.

7.6. Ion exchange resin: Strong cation exchange resin, Amberlite IR-120, or equivalent.

7.7. Stock sulphate solution 1000 mg/l SO_4: In distilled water in a one-litre volumetric flask, dissolve 1.479 g anhydrous sodium sulphate, Na_2SO_4. Make up to the mark with distilled water.

7.8. Standard sulphate solution: Prepare a series of standard solutions by diluting suitable aliquots of stock sulphate solution with distilled water. The concentration of standard solutions are (in mg/l): 0 (blank), 10,20,30,40,50,60,80,100, and 150.

7.9. Standard barium chloride solution: Dissolve 0.4 g barium chloride, $BaCl_2.2H_2O$, in one litre of distilled water which has been adjusted to pH 3.8 - 4.0 with dilute hydrochloric acid or ammonium hydroxide solutions. Standardize following section 8 using standard sodium sulphate solutions (7.8).

8. Procedure

8.1. Pass the sample through the ion exchange column (10-15 ml at a time) discarding the effluent. Repeat this three times. Pipette a 10.0-ml aliquot of the next effluent into a small white casserole dish.

8.2. Add 40 ml alcohol and 2 drops thorin indicator. Adjust the pH to 3.8 - 4.0 by carefully adding, drop by drop, NH_4OH (1:99 solution) until the solution just turns pink. Then add HCl (1:99 solution), drop by drop, until the pink colour disappears; 1 drop is usually sufficient. If the NH_4OH is added too fast, it is possible to overrun the colour change from yellow to pink and the sample continues to be yellow. It is then impossible to develop the pink colour by addition of NH_4OH.

8.3. Titrate with $BaCl_2$ solution until sample just turns pink.

9. Calculations

9.1. The sulphate concentration may be obtained by either of two procedures as follows:

9.1.1. Prepare a calibration curve (ml of barium chloride needed to titrate standard sulphate solutions (7.8)) vs mg/l SO_4, and the sulphate concentration of sample read directly from the graph.

9.1.2. Calculate the sulphate concentration in the sample from the equation:

$$mg/l\ SO_4 = Fx\ (V-B)$$

where F is the "factor" obtained from the titration of the standard sulphate solutions (7.8).

A factor, f, is obtained for each standard solution from

$$f, = \frac{C}{N-B}$$

where C is the concentration of the standard sulphate solution in mg/l SO_4,
N is the volume of barium chloride solution used for the titration, and
B is the volume of barium chloride solution used for the titration of the blank (0.0 mg/l SO_4).

The factor, f, is then obtained by averaging the individual factors obtained for the standard sulphate solutions.

V is the volume of barium chloride solution used to titrate the sample.

B is the volume of barium chloride used to titrate the blank i.e., distilled water.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficient of variation at a sulphate concentration of 25 mg/l SO_4 was ±3.0%.

11. Reference

11.1. American Society for Testing and Materials. 1966. Book of ASTM Standards, Part 23: Industrial Water; Atmospheric Analysis. Philadelphia.

TURBIDITY

(Hach Turbidimeter)

1. Scope and Application

1.1. This method is applicable to the determination of turbidity in surface, ground and waste waters over the range 0 to 1000 Jackson Turbidity Units (JTU). Samples having higher turbidities can be measured by appropriate dilution of an aliquot.

2. Principle of Method

2.1. In the Hach laboratory turbidimeter, a strong light beam is sent upwards through a transparent tube containing the sample and the suspended particles reflect the light. That light which is reflected at 90° to the axis is received by photocells and their electrical response is proportional to the amount received and hence to the sample turbidity. A calibration of the instrument is made using a standard suspension of Formazin - the reaction product of aqueous solutions of hydrazine sulphate and hexamethylene tetramine. Standardization of the instrument utilizes a polyacrylic plastic rod into which a special turbidity material has been cast.

3. Interferences

3.1. In water samples, air bubbles can give false, high readings and the samples must be free from these prior to measurement. With very turbid or highly coloured samples, the meter may read less than the actual amount of turbidity present and hence it should be diluted quantitatively and remeasured using a filtered portion of the same sample for dilution to maintain equilibrium in the suspension. Floating grease and oil may require skimming off prior to measurement.

4. Sampling Procedure and Storage

4.1. Equilibrium conditions may change sufficiently to alter the suspension characteristics of a water sample with time. The measurement should thus be made as rapidly as possible after sample collection.

5. Sample Preparation

5.1. Samples should be well shaken for turbidity measurement.

5.2. See Interferences (3) for precautions to be observed prior to measurement.

6. Apparatus

6.1. Hach turbidimeter model 1860, 2100 or 2100A available from Hach Chemical Company, Ames, Iowa, U.S.A.

6.1.1. The standard for turbidity is a polyacrylic plastic rod with a special turbidity material cast into it which is supplied with the instruments.

7. Reagents

7.1. Stock turbidity suspension, 4000 JTU:

7.1.1. Dissolve 5.000 g hydrazine sulphate, $N_2H_4H_2SO_4$, in about 400 ml distilled water.

7.1.2. Dissolve 50.000 g hexamethylenetetramine in about 400 ml distilled water.

7.1.3. Pour the two solutions (7.1.1. and 7.1.2.) into a one-litre volumetric flask and dilute to volume with distilled water. Allow the solution to stand for 48 hours at 20° to 22°C (68° to 72°F) during which time the suspension will develop. Prepare fresh each month.

7.2. Standard turbidity suspensions: Prepare a series of standards by suitable dilution of the stock turbidity suspension (7.1). Prepare fresh each week.

8. Procedure

8.1. Turn instrument on and allow 30 sec warm-up.

8.2. Insert the standard turbidity rod, and place the light shield over the cell holder.

8.3. Adjust the standardization control on the 0-100 JTU scale for a reading equal to that stamped on one end of the standardization rod. Do not leave the standard turbidity rod in the instrument for long periods while the instrument is turned on.

8.4. The instrument is now standardized. When the range 0-1000 JTU is to be used, the small cell and cell adapter must be used. When using the lower ranges, 0-100, 0-10, 0-1 and 0-0.2 JTU, the large cell must be used.

8.5. To determine turbidity of a water sample, fill the sample cell with a representative portion of sample to within $\frac{1}{4}$ or $\frac{1}{2}$ inch of the top. Adjust the range switch until a reading can be made.

8.6. If sample dilution is required, a filtered portion of the same sample should be used for dilution water to maintain equilibrium conditions.

8.7. The standardization rod should be checked periodically using standard turbidity suspensions in order to ensure the reliability of the rod.

9. Calculations

9.1. The meter reads directly in JTU.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Division), the coefficients of variation at turbidity levels of 1, 10, 40 and 100 JTU were ±9.22, ±3.96, ±1.68, and ±0.45% respectively.

11. References

11.1. Hach Chemical Co. Operation Manual for Hach Laboratory Turbidimeter Model 1860, Ames, Iowa, U.S.A.

11.2. American Public Health Association. 1965. Standard Methods for the Examination of Water and Wastewater. Twelfth Ed., New York.