Applicability of the Technicon
AutoAnalyzer I and II Systems
for Shipboard Analysis of
Great Lakes Water Samples

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Abstract

Water samples from lakes Ontario and Huron were analyzed simultaneously, using the Technicon AutoAnalyzer I and II (AAI and AAII) systems, for soluble reactive phosphate, soluble reactive silica, nitrate plus nitrite nitrogen, ammonia nitrogen, total alkalinity and chloride. This paper describes the major instrumental features of the AAI and AAII systems and compares the results of sample analysis, standard deviations and percent recoveries for the methods used.

The results of the study indicated that comparable analytical results were obtainable from the two systems for all of the parameters except ammonia. The results of sample analysis for ammonia by the AAI method exceeded those obtained using the AAII method by as much as 18%. Both systems gave satisfactory percent recoveries and the precisions compared reasonably well.

Résumé

Des échantillons d'eau des lacs Ontario et Huron ont été analysés simultanément à l'aide des appareils auto-analyseur Technicon I et II (AAI et AAII), pour en déterminer les teneurs en phosphates solubles réactifs, en silice soluble réactive, en azote nitrique et nitreux, en azote ammoniacal et en chlorures, ainsi que l'alcalinité totale. Le présent rapport décrit les caractéristiques principales des appareils AAI et AAII, et compare les résultats des analyses, l'écart type et le rendement de récupération des méthodes utilisées.

L'étude a montré que les deux types d'appareils permettaient un dosage équivalent de tous les paramètres sauf l'azote ammoniacal. Dans ce dernier cas, les résultats obtenus en utilisant l'appareil AAI dépassaient de 18% ceux de l'autre. Le rendement de récupération obtenu par les deux dispositifs était satisfaisant et leur précision comparable.

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INTRODUCTION

The Technicon AutoAnalyzer (AAI and AAII) systems are now widely used for the analysis of water and wastewaters of various types. To date, most of the analytical data collected by the Water Quality Branch Laboratory at Canada Centre for Inland Waters in support of Great Lakes studies have been acquired by use of the AAI systems. The AAII systems introduced improved analytical techniques in the autoanalyzer field. It was necessary, therefore, to check for compatibility of analytical results obtained by both systems to ensure data consistency. Such an evaluation was undertaken by the authors to assess and compare the performances of the systems for shipboard analysis of Great Lakes water samples with the intent of replacing the AAI systems with AAII systems.

During the 1972-1973 field year, two triple-channel Technicon AAII systems were installed in the Water Quality Laboratory aboard the MV MARTIN KARLSEN, and filtered water samples from lakes Ontario and Huron were analyzed.

INSTRUMENTAL FEATURES

There are a number of salient features incorporated in the AutoAnalyzer II modules that make them more advantageous than those of the AutoAnalyzer I for water analysis. The AAII systems facilitate more rapid sample analysis and data acquisition. The programmable sampler IV, which eliminates the use of the less precise and less flexible cams (Varley and Baker, 1971; Davidson, Mathieson and Boyne, 1970; Young, Montagne and Snider, 1968), is indeed a vast improvement upon the AAI sampler II. The damping and range expansion devices incorporated in the AAII colorimeter permit lower detection limits and are useful features, particularly for Great Lakes water analysis. Adjustable apertures and the easy adaptability to flow cells of varying path lengths allow much greater flexibility of the colorimeter. Also the two-channel optical system permits automatic correction for non-related colour interferences by allowing the blank stream through the reference channel.

Generally, the advanced features incorporated in the AAII modules, such as samplers, proportioning pumps, cartridges, linearizers, sample identification (IDEE*), data converters, recording and printing devices, all enable quicker acquisition of analytical data of excellent quality. For example, in the case of the AAII digital printer, sample concentrations can be read directly from the printer-readout, and the data system could be easily computerized if required. Thus, the handling and analysis of large quantities of data are far less tedious. Also, the AAII system permits a more precise interpretation of sample peaks than is possible from the AAI system.

The compactness of some of the AutoAnalyzer II components is another advantage in its applicability to shipboard analysis. The AAII components such as dialyzers, heating baths, and time delay and mixing coils are all of reduced sizes compared to the AAI components and are neatly contained in a single cartridge. Much smaller reagent and sample volumes are required for the AAII systems than for the AAI systems. The use of cartridges is advantageous in that with the wide temperature variations likely to be experienced in the shipboard laboratory, better temperature control is possible within the AAII system than with the conventional AAI manifolds (Grasshoff, 1969). Another useful feature of the AAII system is in the proportioning pump III. The capability of the end blocks to accommodate almost twice as many pump tubes than is possible with the AAI pump results in a reduction of the number of pumps required for multi-channel systems.

METHODOLOGY

The AAII systems, suitable for both linear and non-linear chemistries, measure optical density after completion of the reaction and colour changes, whereas in the AAI systems, optical density may not necessarily be measured at the steady state (Varley and Baker, 1971). The air injection and the addition of a wetting agent are essential factors for satisfactory performance in the application of the AAII systems. Figures 1 to 6 show the manifolds used,

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* Technicon trademark

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and the procedures for reagent preparation are given in the Appendix. The AAI manifolds were identical to those reported by Philbert and Traversy (1973). The chemistries of the AAI and AAII methods were generally similar except in the case of ammonia for which the AAI ortho-tolidine method was used. A prime factor in the selection of methods was that they were to be sensitive enough to detect low concentrations of constituents in Great Lakes water with a minimum number of problems.

The Technicon Industrial AAII method No. 108-71W for "The Determination of Low Level Ammonia in Fresh and Estuarine Waters" (Technicon Instruments Corp., 1971) was tried and modified (Fig. 4). The AAII alkaline phenol method proved to be simpler and much more reliable than the AAI ortho-tolidine method for determining low-level ammonia.
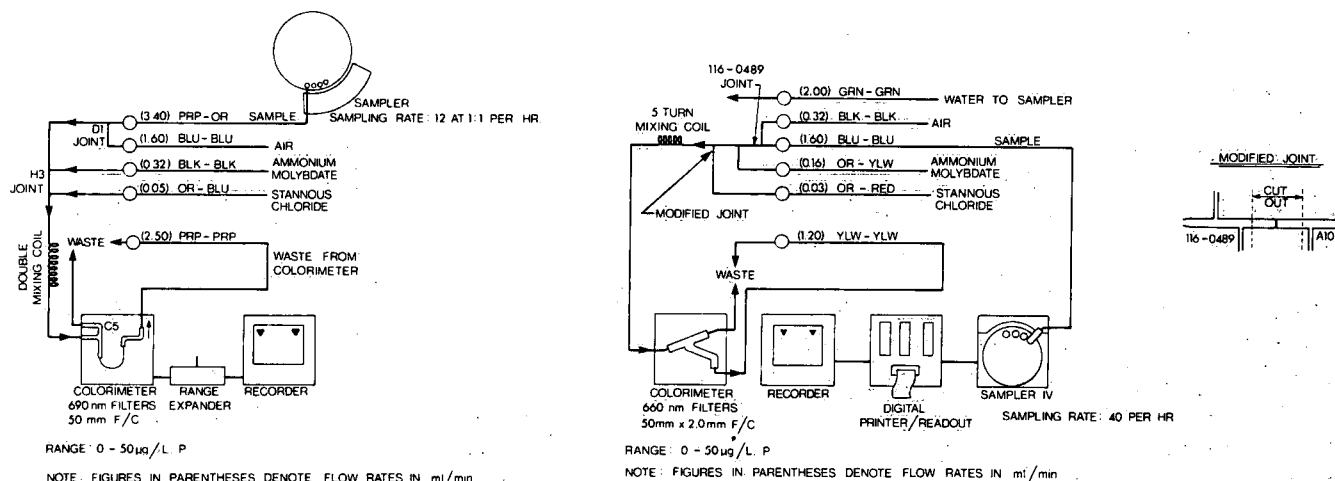

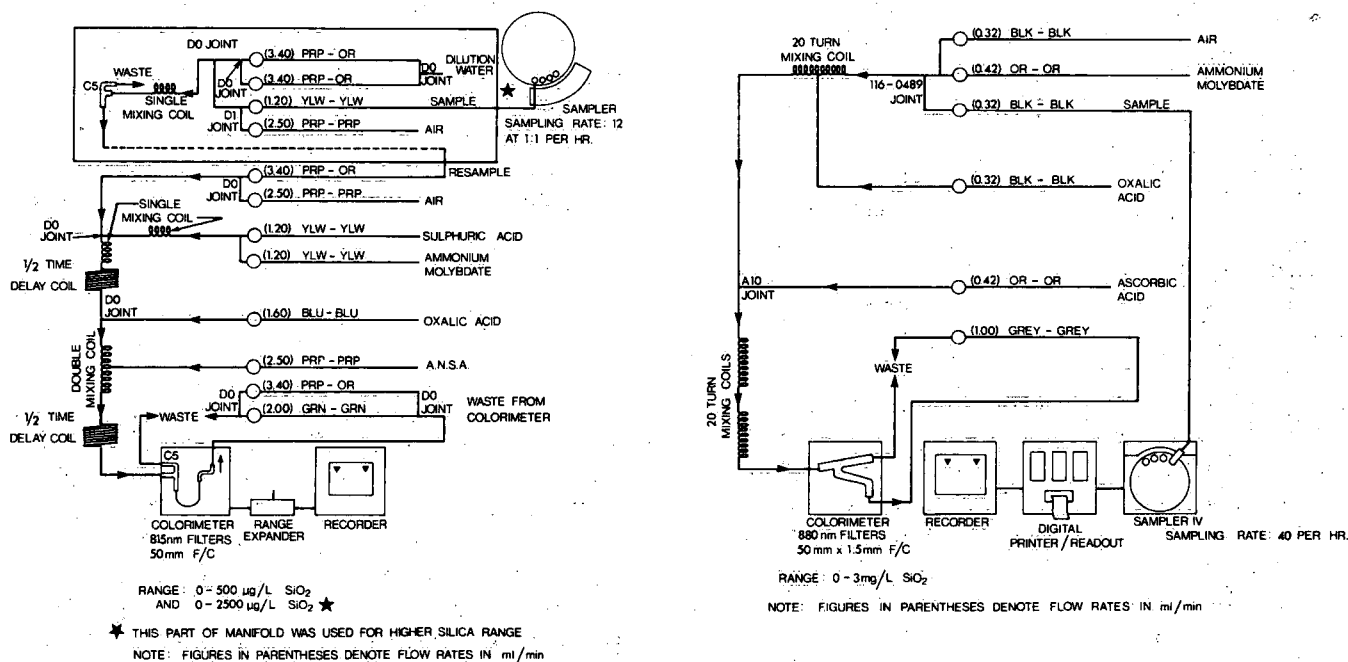**Figure 1.**　　**Phosphorus AAI and AAII manifolds.**

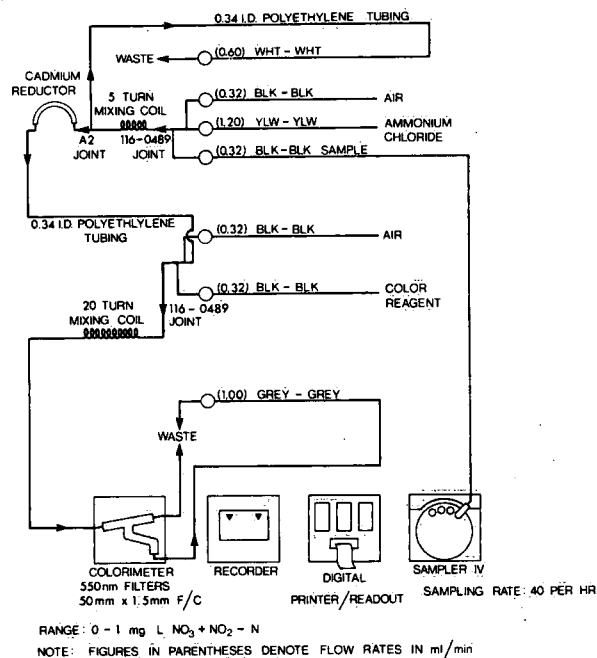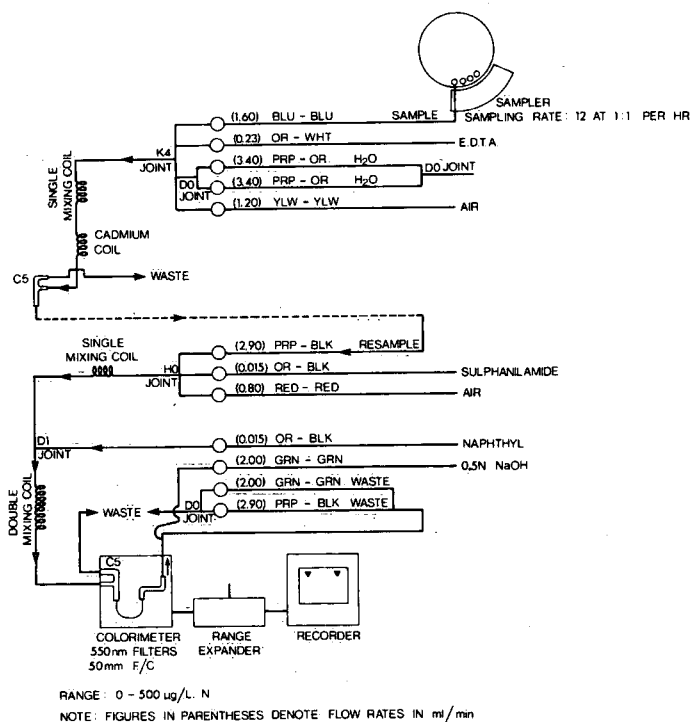**Figure 2.**　　**Silica AAI and AAII manifolds.**

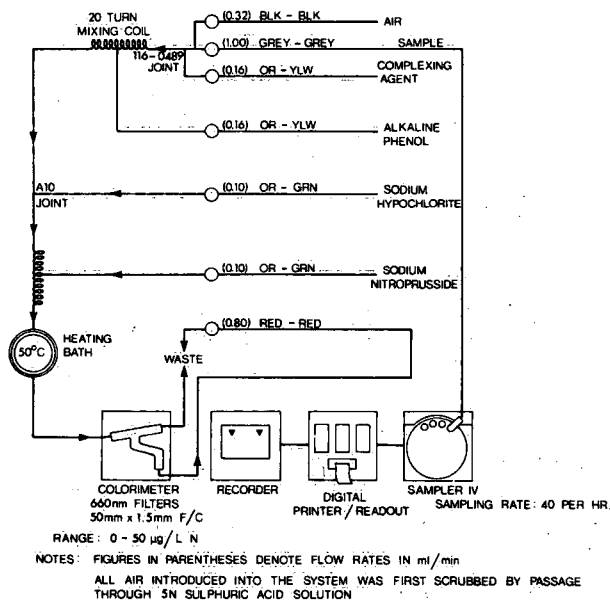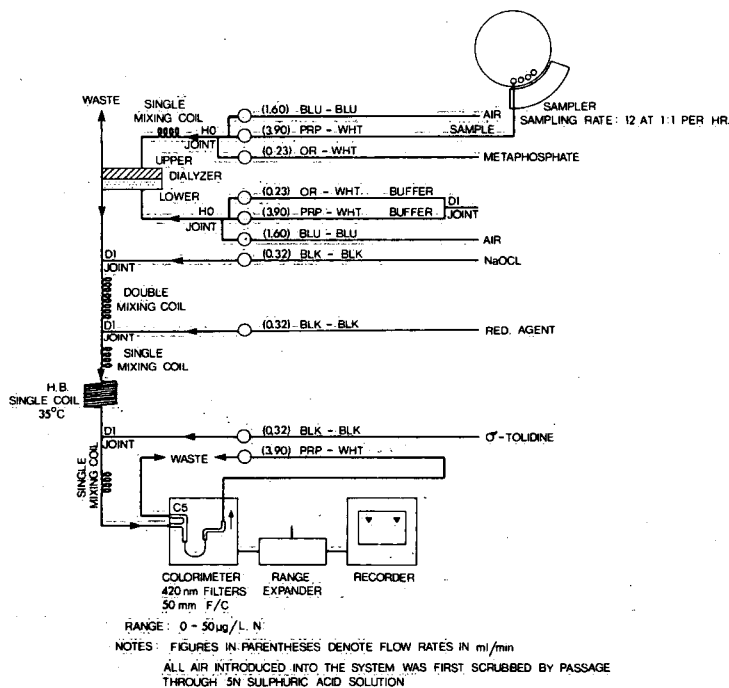**Figure 3.** Nitrate plus nitrite AAI and AAII manifolds.
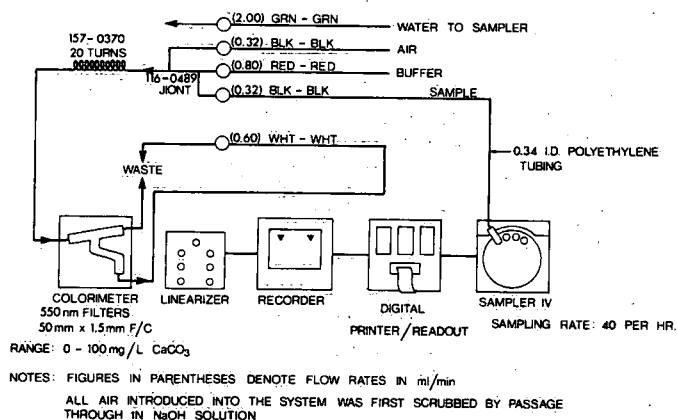

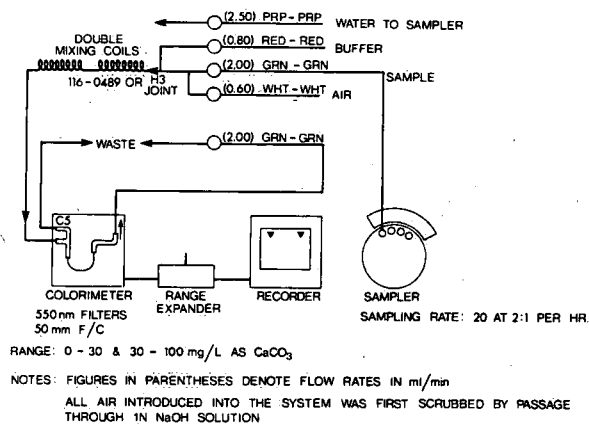**Figure 4.** Ammonia AAI and AAII manifolds.

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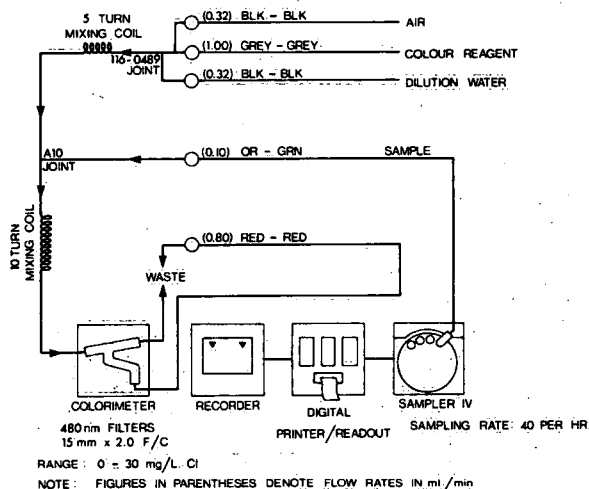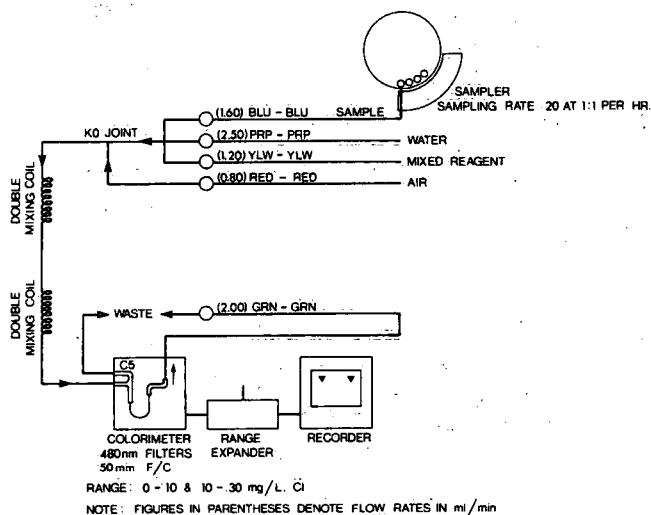**Figure 5.** Total alkalinity AAI and AAII manifolds.

Figure 6. Chloride AAI and AAII manifolds.

The Technicon Preliminary Industrial AAII ascorbic acid method No. 155-71W (Technicon Instruments Corp., 1971) for phosphate was tried, but many problems were encountered. For example, there was a continuous base-line drift when standards within a range of 0-40 μg P/l were run. Furthermore, the method had a detection limit of 4 μg P/l and lacked the sensitivity for phosphorus measurements in the low concentration ranges of interest. The Levor IV concentration was increased to 3 ml/l and the ascorbic acid and acid molybdate solutions of the mixed working reagent suggested by Technicon were fed separately into the manifold. This yielded promising results at first. With a

standard calibration setting of 0.5, a 40 μg P/l standard gave full-scale deflection with stable base line. This method, however, proved to be far too susceptible to silica interference for the concentration range normally found in Great Lakes waters. A solution (pH 7) containing 500 μg SiO_2/l gave a peak comparable in height to that of a 40 μg/l phosphorus standard. The sulphuric acid concentration in the ammonium molybdate reagent was increased in five-millilitre increments from 75 ml/l to 95 ml/l. Although silicia interference was reduced, phosphorus sensitivity was decreased drastically. Finally the decision was made to adapt the stannous chloride method to the AAII system (Fig. 1).

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Table 1. Average Recoveries, Standard Deviations and Coefficients of Variation for AAI and AAII Systems

Parameter	Percent recovery (mean)		Standard deviation (mean)		Coefficient of variation (%)	
	AAI	AAII	AAI	AAII	AAI	AAII
Soluble reactive (ortho) phosphate	100	100	0.32 $\mu g/l$ @ 15.8 $\mu g/l$	0.31 $\mu g/l$ @ 17.9 $\mu g/l$	2.0	1.7
Soluble reactive SiO_2	98	101	6.8 $\mu g/l$ @ 140 $\mu g/l$	3.5 $\mu g/l$ @ 140 $\mu g/l$	4.9	2.5
Nitrate + nitrite - N	98	98	3.4 $\mu g/l$ @ 195 $\mu g/l$	1.7 $\mu g/l$ @ 192 $\mu g/l$	1.8	0.88
Ammonia - N	103	99	0.66 $\mu g/l$ @ 31 $\mu g/l$	0.48 $\mu g/l$ @ 33 $\mu g/l$	2.1	1.4
Total alkalinity as $CaCO_3$	99	99	0.36 mg/l @ 91.0 mg/l	0.64 mg/l @ 90.8 mg/l	0.39	0.70
Chloride - Cl	96	100	0.13 mg/l @ 26.5 mg/l	0.12 mg/l @ 26.5 mg/l	0.49	0.45

RESULTS AND DISCUSSION

Recoveries, standard deviations and coefficients of variation are shown in Table 1. These values are averages of several determinations made by different analysts during the field season. Standard deviation was determined by replicate sample analysis.

Analytical results from the respective systems were compared by conducting concurrent analysis on a large number of sample pairs collected throughout the field season from various locations in both lakes and by applying the t-test to determine significant differences at the 95% confidence level (Dixon and Massey, 1969). It should be noted that the analytical data from the AAI systems were subjected much more to human influence and rounding off than in the case of data generated from the AAII systems.

The results indicated very satisfactory agreement of analytical data for soluble reactive phosphate, silica, nitrate plus nitrite, total alkalinity and chloride. There was a strong positive bias in the results of ammonia analysis by the AAI method. Generally, ammonia values from the AAI method exceeded those from the AAII method by as much as 18% for concentrations close to the 10 $\mu g/l$ ammonia-nitrogen level.

No significant differences were observed when samples were analyzed in parallel for reactive phosphate by AAI and AAII stannous chloride methods. Yet comparison of soluble reactive phosphate data from the AAI stannous chloride and AAII ascorbic acid methods revealed that for water samples containing an average of 575 μg SiO_2/l and 13.8 μg P/l, the ascorbic acid method yielded results averaging as much as 43% higher than those from the AAI stannous chloride method. This may have been a direct result of silica interference in the ascorbic acid method (Coote, Duedall and Hiltz, 1970; Campbell and Thomas, 1970).

CONCLUSION

Comparable results are obtainable for soluble reactive silica, nitrate plus nitrite nitrogen, total alkalinity and chloride using the AAI and AAII systems. Ammonia data from the AAI method were considerably higher than data obtained by the AAII method. Comparable results for soluble reactive phosphate were obtained only when the stannous chloride method was used in both cases. The respective standard deviations and percent recoveries of the AAI and AAII methods compared reasonably well, but the AAII method afforded faster and less tedious sample analysis and data handling. The possibility of human error in data handling was reduced with use of the AAII system.

The Technicon AutoAnalyzer II, owing to its many new features, proved to be a more preferable analytical system than the AAI system in its applicability to shipboard analysis of Great Lakes water samples.

ACKNOWLEDGMENT

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PREPARATION OF REAGENTS USING AAI METHOD

Phosphorus

Ammonium Molybdate (1.25%)

A) In 500 ml deionized-distilled water dissolve 12.5 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$.

B) Dilute 77.5 ml concentrated sulphuric acid to 500 ml with deionized-distilled water and cool. Mix solutions A and B.

Stannous Chloride

Stock Solution — Dissolve 1.2 g stannous chloride $(SnCl_2.2H_2O)$ in 100 ml concentrated hydrochloric acid. (It is stable for about two weeks if stored at approximately 4°C).

Working Solution — Dilute 5 ml of stock solution to 100 ml with deionized-distilled water. (It is stable for about five to eight hours).

The same reagents are used for total phosphorus determination except that the wash water contains 12 ml of concentrated H_2SO_4 per litre.

Nitrate Plus Nitrite

Sulphanilamide (1%)

Dissolve 10 g sulphanilamide $(4-NH_2C_6H_4SO_2NH_2)$ in a mixture of 100 ml concentrated hydrochloric acid and 900 ml deionized-distilled water.

Naphthyl Reagent (0.1%)

Dissolve 1 g N-1-Naphthylethylenediamine dihydrochloride $(C_{10}H_7NH.CH_2.CH_2.NH_2.2HCl)$ in 1 litre deionized-distilled water and store in an amber bottle.

E.D.T.A. (2.5%)

In 900 ml deionized-distilled water dissolve 25 g ethylenediaminetetra-acetic acid (disodium salt $[(CH_2.N(CH_2.COOH).CH_2.COONa)_22H_2O]$ and adjust pH to 6.5-7.0 with a 10% sodium hydroxide solution. Make solution up to 1 litre with deionized-distilled water.

Cadmium Reducing Column

Loosely pack cadmium filings (No. 20 mesh) into glass or pump tubing of suitable length and bore. The filings may be held in place by means of glass wool plugs and nipples.

Ammonia

Alkaline Metaphosphate

A) Dissolve 20 g sodium metaphosphate $[(NaPO_3)_6]$ in 1 litre deionized-distilled water.

B) Dissolve 26 g sodium hydroxide in 1 litre deionized-distilled water. Mix equal volumes of solutions A and B before use.

Buffer

Dissolve 95 g disodium hydrogen orthophosphate (Na_2HPO_4) and 7.5 g sodium dihydrogen orthophosphate $(NaH_2PO_4.H_2O)$ in 20 litres deionized-distilled water. Filter.

*Sodium Hypochlorite* (0.004% available chlorine)

Dilute 1 ml sodium hypochlorite (NaOCl), containing 4% available chlorine, to 1 litre with deionized-distilled water.

Reducing Agent

Dissolve 340 g monochloracetic acid $(CH_2Cl.COOH)$ and 40 g oxalic acid $[(COOH)_2.2H_2O]$ in 2 litres deionized-distilled water.

Acid σ-Tolidine (0.12%)

In 120 ml concentrated hydrochloric acid dissolve 1.2 g σ-tolidine dihydrochloride

$$[NH_2.C_6H_3(CH_3).C_6H_3(CH_3)NH_2.2HCl]$$
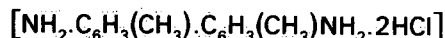
and dilute to 1 litre with deionized-distilled water. Filter and store in an amber bottle.

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Silica

Ammonium Molybdate (2%)

In 2 litres deionized water dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$.

Sulphuric Acid (0.2N)

Dilute 11.1 ml concentrated sulphuric acid to 2 litres with deionized water.

Oxalic Acid (5%)

Dissolve 100 g oxalic acid $[(COOH)_2.2H_2O]$ in 2 litres deionized water.

A.N.S.A.

Stock Solution — Dissolve 150 g sodium bisulphite $(NaHSO_3)$ and 5 g anhydrous sodium sulphite (Na_2SO_3) in 800 ml deionized water. Heat to 50°C and add 2.5 g of 1-amino-2-naphthol-4-sulphonic acid

$$[NH_2C_{10}H_5(OH).SO_3H]$$
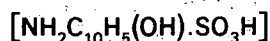
and stir until almost completely dissolved. Dilute to 1250 ml with deionized water and filter. Store in an amber bottle.

Working Solution — Dilute 100 ml of stock solution to 1 litre with deionized water.

Chloride

A) Ferric Alum (6%)

In 250 ml deionized-distilled water dissolve 60 g ferric ammonium sulphate $[NH_4Fe(SO_4)_2.12H_2O]$ and add 380 ml concentrated nitric acid. Make up to 1 litre with deionized-distilled water.

B) Mercuric Thiocyanate (Saturated)

Dissolve 1 g mercuric thiocyanate $[Hg(SCN)_2]$ in 1 litre deionized-distilled water. Stir for approximately 1 hour.

Mixed Reagent

Add 1 part of solution A to 3 parts of solution B. Mix and filter before use.

Total Alkalinity

Buffered Indicator

In a little ethanol dissolve 0.05 g methyl orange $[(CH_3)_2NC_6H_4.N:NC_6H_4SO_3Na]$. Add 1 litre deionized-distilled water followed by 2.0423 g potassium hydrogen phthalate $(COOH.C_6H_4.COOK)$. Stir until dissolved and add approximately 35 ml 0.1N hydrochloric acid. Dilute to 2 litres and adjust the pH to 2.65-3.10 depending on range

PREPARATION OF REAGENTS USING AAII METHOD

Phosphorus

Ammonium Molybdate (1.19%)

A) In 500 ml deionized-distilled water dissolve 11.9 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$.

B) Dilute 73.8 ml concentrated sulphuric acid to 500 ml with deionized-distilled water and cool. Mix solutions A and B.

Stannous Chloride

Stock Solution (1.2%) — Dissolve 1.2 g stannous chloride $(SnCl_2.2H_2O)$ in 100 ml concentrated hydrochloric acid. (It is stable for about two weeks if stored at about 4°C.)

Working Stannous Chloride-Hydrazine Sulphate Solution — Add 10 ml of a hydrazine sulphate solution containing 2 g/100 ml to 85 ml deionized-distilled water. Add 0.7 ml Levor IV and mix thoroughly. Add 4 ml stock stannous chloride in aliquots of about 0.5 ml, mixing thoroughly after each addition. The reagent should be free of colour and/or turbidity.

Nitrate Plus Nitrite

Ammonium Chloride

Adjust the pH of deionized water to 8.5 with a dilute ammonia solution and then dissolve 10 g ammonium chloride. Make up to 1 litre and add 0.5 ml Brij-35.

Colour Reagent

Dilute 200 ml orthophosphoric acid to 1500 ml with deionized water. Dissolve 20 g sulphanilamide, and 1 g N-1-Naphthylethylenediamine dihydrochloride, and make to 2 litres. (This reagent is stable for four weeks if kept in a cool dark place.)

Cadmium

Use coarse cadmium powder (T11-5063*). Wash with a little 1N-HCl followed by deionized water to remove grease and oil. Air dry and store in a well-sealed bottle.

Cadmium Reductor Column

Use a purple pump tube (0.081 in. ID). Wash 10 g of cadmium with 50-millilitre aliquots of 2% w/v copper sulphate solution until no blue colour remains in solution and semi-colloidal copper particles begin to enter the supernatent liquid. Wash thoroughly with distilled water to remove all traces of this colloidal copper. Fill the purple pump tube completely with water and using a Pasteur pipette displace the water with the cadmium filings. When full, plug (loosely) both ends with glass wool. Never allow air to enter this column. It is wise to store these columns under water when not in use. When the column has lost its reductive power, it may be washed with HCl and $CuSO_4$ as above and reused.

Ammonia

Complexing Reagent

Dissolve 1.65 g potassium sodium tartrate ($KNaC_4H_6O_6.2H_2O$) and 1.2 g sodium citrate dihydrate in 950 ml deionized water. Adjust pH to 5.0 with H_2SO_4 and make to 1 litre.

Alkaline Phenol

Dissolve 21 g of phenol in 50 ml deionized water and cool. Cautiously add 180 ml of 5% w/v sodium hydroxide solution. Dilute to 1 litre.

Sodium Hypochlorite (0.26% available chlorine)

Dilute 50 ml of stock hypochlorite, having 5.25% available chlorine to 1 litre with deionized water.

Sodium Nitroprusside

Dissolve 0.25 g sodium nitroprusside and make to 1 litre with deionized water.

Silica

Ammonium Molybdate (2%)

A) In 1 litre deionized water dissolve 20 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$.

Sulphuric Acid (0.2N)

B) Dilute 5.5 ml concentrated sulphuric acid to 1 litre with deionized water. Mix equal volumes of solutions A and B. Add 0.5 ml Levor IV per litre.

Oxalic Acid (5%)

Dissolve 50 g oxalic acid $[(COOH)_2 2H_2O]$ in 1 litre deionized water.

Ascorbic Acid (1.86%)

In deionized water dissolve 17.6 g ascorbic acid $[O.CO.C(OH):C(OH).CH.CH(OH).CH_2OH]$. Add 50 ml acetone and dilute to 1 litre with deionized water. Add 0.5 ml Levor IV.

Chloride

A) Ferric Nitrate (20.2%)

Dissolve 202 g ferric nitrate $[Fe(NO_3)_3.9H_2O]$ in deionized water. Add 22.5 ml concentrated nitric acid and dilute to 1 litre with deionized water.

B) Mercuric Thiocyanate (0.417%)

Dissolve 4.17 g mercuric thiocyanate $[Hg(SCN)_2]$ in 1 litre methanol and filter.

Mixed Reagent

Mix 300 ml of solution A and 1 litre of water with 300 ml of solution B and dilute to 2 litres.

Total Alkalinity

pH 3.1 Buffer

Dissolve 10.2 g potassium hydrogen phthalate in 500 ml deionized water. Using 1N-HCl adjust the pH to 3.1 and make to 1 litre.

* Technicon number

Methyl Orange Indicator

Dissolve 0.5 g methyl orange powder in deionized water and make to 1 litre. Filter if necessary.

Buffered Indicator

Add 85 ml of methyl orange solution to 250 ml of pH 3.1 buffer and dilute to 2 litres. Add 1.0 ml Brij-35.