THE CHEMICAL ANALYSIS OF FRESH WATER

By
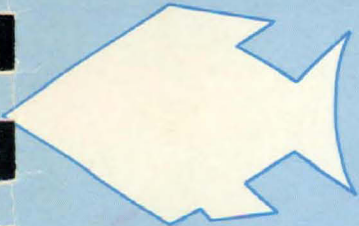M.P. STAINTON
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ABSTRACT

STAINTON, M.P., M.J. CAPEL, and F.A.J. ARMSTRONG. 1977.

The Chemical Analysis of Fresh Water, 2nd ed.

Fish. Mar. Serv. Misc. Spec. Publ. 25:166 p.

This publication describes analytical methods used in the
Freshwater Institute for the chemical analysis of fresh water.
Emphasis is on the determination of carbon, nitrogen, phosphorus
and silicon in dilute waters. Recommendations are made concerning
sampling techniques, sample manipulation and storage. Estimates of
analytical precision are included.

RÉSUMÉ

STAINTON, M.P., M.J. CAPEL, and F.A.J. ARMSTRONG. 1977.

The Chemical Analysis of Fresh Water, 2nd ed.

Fish. Mar. Serv. Misc. Spec. Publ. 25:166 p.

Le présent ouvrage décrit les méthodes analytiques employées
à l'Institut des eaux douces pour l'analyse chimique de l'eau douce.
On spécialise dans la détermination du carbone, de l'azote, du
phosphore et du silicium, en solutions diluées (en faibles concentrations).
On inclut des recommandations relativement aux techniques d'échantillonage,
à la transformation des echantillons et à leur entreposage. On estime la
précision analytique.

ACKNOWLEDGMENTS

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INTRODUCTION

These methods have been in use in this Institute for some time, for analysis of fresh waters, mostly of low solute content, and often highly coloured. Care should be taken in applying them to alkaline, hard, or saline waters, although many are adaptations of methods for sea water.

They have been used mainly in studies of aquatic productivity and are therefore mostly for determination of micronutrients rather than for pollutants or assessment of water quality. They are not intended in any way as standard methods, and can be modified as experience demands, if they can be made to yield results closer to what is actually present.

None of them should require any great analytical skill, and we have tried to lay out the instructions as simply as possible, and to keep theory and explanatory matter to the minimum. It is, of course, to the advantage of the analyst, and especially to the supervisor, to get all the background knowledge available, and we recommend reference to the sources mentioned with the methods, and to the texts listed below. Our own indebtedness to these sources should be obvious. In choosing among methods we have gone for simplicity and speed, partly for greater productivity in a busy laboratory, but also because the longer an analysis takes, and the more manipulation

there is, the greater the chances of contamination.

We have evaluated errors of analysis at one or more levels for most of these methods, and so have an indication of the precision in replication from a single sample. Sampling error, that is the variability of separate samples taken successively from the same spot, is another matter. It is known, for example, that the suspended matter in a lake, or the phyto- or zooplankton, may be patchily distributed so that analyses of successive samples, even if quickly taken, may show a relative standard deviation of ±20% or more. When interpreting analyses of particulate material, it would be wise to test for significance.

We have generally used research type instruments for our own analyses, because these are what we use in developing methods and we have them and are familiar with them. Some methods are laid out for use with specified instruments, but are adaptable to others. Much can be done with simpler instruments, and good absorptiometric work does not necessarily demand instruments with monochromators, double beam systems, or strip-chart or digital read-out. The laboratory with limited means should be able to work with a filter absorptiometer for most of these determinations if care is taken to choose the correct filter each time. Sophisticated instrumentation will not compensate for errors of timing, contamination or incorrect storage of samples.

At summer temperatures changes in nutrient concentrations can be rapid, as bacteria or phytoplankters multiply, and storage for 24 hours

can make analyses meaningless. Generally, changes can be arrested by freezing and keeping samples frozen until analyzed, though this can upset silicate analyses, and probably those for calcium and magnesium as well. Methods of storage are indicated for each determination.

Usually analyses are done on filtered samples. If the suspended matter is also analyzed, some constituents can be assigned to "dissolved" or "suspended" fractions. The distinction is, of course, an artificial one and has to depend on the porosity of the filter used. To have some physical meaning, the dividing line, in particulate size, between particulate and dissolved matter could reasonably be put between 0.1 and 1.0 μm, where the smaller particles might be kept from settling by Brownian movement. Recently there has been a tendency to specify membrane filters of A.P.D. 0.45 μm. However, most cellulose ester membrane filters of this porosity are slow and apt to clog. We prefer Whatman GF/C glass fiber filters, which are faster, and being inorganic and able to be ignited before use, may be used for carbon and nitrogen determination. Although the pore size is greater, and not so well defined, the manufacturers state that 98% of particles between 0.5-1.0 μm are retained. There is very little difference in the quantity of suspended matter retained by these filters, compared with membrane filters of 0.45 μm A.P.D.

We will greatly appreciate correspondence from users of these methods, indicating errors or difficulties with any of them, and suggesting improvements. It is our intention to update the manual

annually. Those wishing to receive these supplements should fill out the
information form provided inside the back cover.

SELECTED REFERENCES

American Public Health Association. 1971. Standard methods for the
examination of water and waste water. 13th ed. APHA, New York,
N.Y. 878 pp.

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of sea water analysis. Bull. Fish. Res. Board Can. 167:311 pp.

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Series Monograph No. 2. Society for Analytical Chemistry,
London, 188 pp.

* New editions are in preparation

SAMPLE COLLECTION

Because of the dilute nature of much of Canadian fresh water, gross changes in sample composition can arise through contamination from sampling equipment, personnel, and from poor sampling technique. Below are listed recommendations concerning samplers, sample containers, and special sampling techniques and precautions.

Using the methods we have described, about 1 liter of water is required for complete analysis (500 ml if automated techniques are used).

Samplers

Two types of sampler have been found useful for work with lakes and slow moving rivers. The 2-liter van Dorn type sampler constructed of clear plastic is an excellent general purpose instrument; easy to load and trigger under all weather conditions and light enough for work in remote areas. Being transparent, this sampler permits viewing samples prior to transfer to sample bottles which is essential when sampling near the sediment-water interface.

For shallow lakes and situations where good resolution of stratification is required, a 12 volt D.C. peristaltic pump has some advantage. Little turbulence in the source occurs with this sampler, as only a small diameter weighted tube is lowered to the desired depth. However, this equipment is heavy and cannot be used for winter sampling.

Sample Bottles

We have found the 500 ml translucent polyethylene screw-cap
bottle to be the most useful sample container for field use. Poly-
propylene appears to be too brittle, particularly at low temperatures,
to be serviceable. Opaque sample bottles should be avoided, it being
quite difficult to tell when they are clean. Before use, bottles
should be washed with a phosphate-free detergent, followed by rinses
with dilute hydrochloric acid and distilled and deionized water. When
attempting to measure trace nutrients and metals the effect of sample
container walls must be investigated.

When sampling, bottles should be rinsed twice before filling.
Samples should not be stored in polyethylene sample bottles for more
than a few days as bacterial films form on bottle walls. These films
are difficult to remove and may contaminate subsequent samples.

Special Techniques and Precautions

Dissolved oxygen

It is essential to minimize contact between the sample and
atmosphere. If a van Dorn type sampler is used it must be
equipped with a 12"-18" flexible tube to dispense sample.
Samples must be collected in specially designed glass "B.O.D."
bottles having conical stoppers to prevent bubble entrapment.

When transferring sample the sampler dispensing tube must be placed at the bottom of the sample bottle and held below the liquid surface while filling. At no time should sample be allowed to cascade into the bottle. Liquid should be allowed to overflow the bottle by at least one bottle volume. The bottle should then be quickly stoppered, taking care not to trap any air bubbles.

Nutrient elements

When sampling for nutrient elements the usually low levels involved make contamination a significant problem. While the need for clean samplers and sample bottles is obvious there are several other contamination sources which must be avoided. Small amounts of tobacco ash, dandruff and perspiration contributed by field personnel, or plant pollen and other atmospheric particulates all can introduce significant errors into nutrient element analysis. Field personnel must be made aware of these and other possible sources of contamination.

Silicon

Samples collected for silicon analysis must not be stored in glass containers, particularly if they are alkaline. Samples should never be allowed to freeze, as the freeze concentration which occurs in the sample bottle causes precipitation of silicon in a form which does not quantitatively redissolve on thawing.

Deoxygenated waters

When sampling anaerobic waters for dissolved iron, manganese, sulphide and phosphate, it is important, if not essential, to avoid exposure of samples to oxygen prior to analysis. Exposure to oxygen at the least will oxidize ferrous, manganous and sulphide species and will usually precipitate metal oxides and coprecipitate phosphorus. Samples should be treated as for dissolved oxygen with all manipulations and additions of reagents achieved without exposure to atmosphere. Samples should be collected in dissolved oxygen bottles or glass syringes. For metals analysis samples should be filtered and acidified as soon as possible after sampling. For sulphide determination colorimetric reagents are added directly to the sampling syringe.

Dissolved methane

Samples are collected using a peristaltic pump having a pickup tube made of thick walled Tygon ^{R} tubing. The tubing is lowered to depth by addition of half meter or one meter lengths of Tygon ^{R} tubing equipped with tapered polyethylene connectors. This procedure is necessary to avoid coils in the tubing where sample degassing will occur. Samples are pumped directly into glass stoppered 125 ml reagent bottles. At least twice the volume of the bottle is displaced to prevent atmospheric contact. If degassing is likely, 25 ml

of sample is pumped into a 50 ml glass syringe. The syringe is
temporarily sealed with a 26 G needle with the tip inserted into
a small rubber stopper. For extremely precise depth profiles, the
sampler described by Rudd and Hamilton (1976) is recommended.

SELECTED REFERENCES

Rudd, J.W.M., and R.D. Hamilton. 1976. Two samplers for monitoring
dissolved gases in lake water and sediments. Limnol. Oceanogr.
20:902-906.

SAMPLE HANDLING

We have found it useful, and often essential, to filter samples as soon as possible (within hours) after collection. This permits analytical distinction between dissolved and particulate phases and minimizes changes in sample composition arising from biological uptake and excretion. Since parameters differ in their storage condition and time limits it is useful to sub-divide a sample into different containers, each receiving appropriate storage treatment. The sample handling scheme found useful in our laboratories appears in Figure 1.

Three particulate samples are obtained, one each for: chlorophyll, particulate solids and/or particulate phosphorus and particulate carbon and nitrogen. Filtrate is divided into two portions. One is acidified and used for cation analysis; the other is used for nutrient elements, major anions and dissolved solids. A portion of sample remains unfiltered for analysis of ammonia, carbon dioxide, conductivity, pH and soluble reactive silicon.

Dissolved and particulate phases are arbitrarily defined by what passes through or is retained on a pre-ignited (16 hours @ 550 C) Whatman 42.5 mm GF/C glass fiber filter.

SAMPLE HANDLING SCHEME FOR UNFILTERED WATER

```
                    ┌──────────────────────────────┐
                    │     AMMONIA NITROGEN          │
                    │ DISSOLVED INORGANIC CARBON    │
                    │        CONDUCTIVITY           │
                    │   SOLUBLE REACTIVE SILICON    │
                    │ HYDROGEN ION CONCENTRATION    │
                    │   SULPHIDE  & METHANE         │
                    └──────────────────────────────┘
                                  ▲
                                  │
                            UNFILTERED

                         ┌──────────────┐
                         │   SAMPLE     │
                         └──────────────┘
                                  │
                             FILTERED
```

| THROUGH IGNITED PREWEIGHED WHATMAN GF/C FILTER. FILTER DRIED AND USED FOR ANALYSIS OF SUSPENDED SOLIDS AND SUSPENDED PHOSPHORUS | THROUGH IGNITED WHATMAN GF/C FILTER. FILTER PLUS PARTICULATE USED FOR ANALYSIS OF CHLOROPHYLL | THROUGH IGNITED WHATMAN GF/C FILTER FILTER PLUS PARTICULATE DRIED AND ANALYSED FOR SUSPENDED C AND N |

FILTRATE

| DISSOLVED ORGANIC CARBON NITRATE AND NITRITE NITROGEN TOTAL DISSOLVED NITROGEN SOLUBLE REACTIVE PHOSPHORUS TOTAL DISSOLVED PHOSPHORUS CHLORIDE AND SULPHATE TOTAL DISSOLVED SOLIDS | MAJOR CATIONS |

FIGURE 1.

SAMPLE STORAGE

Table I lists guidelines for the treatment and storage of
samples and is a summary of recommendations made within the text of
individual methods. While several preservation methods have been
reported (Hellwig 1963, Brezonik and Lee 1966) and widely used, none
are satisfactory for preserving samples for all analyses. For
determinations of nutrient elements we have found no substitute for
rapid analysis. Where sample storage is necessary samples should, at
the very least, be refrigerated (5 C) but more preferably filtered
and refrigerated, filtered and frozen or filtered and preserved with
mercuric chloride. Choice of preservation technique of course depends
upon the analysis of interest and the water type.

Freezing samples inevitably produces a freeze concentration
causing precipitation of silicon in neutral to acidic waters and metal
salts in alkaline waters. These precipitates often do not
quantitatively redissolve on thawing. Addition of mercuric chloride
to samples interferes with both nitrate and chloride analysis.

The permissible storage times listed in Table 1 are guidelines
only, being a compromise between desirable and possible time limits.
It should be obvious that sample deterioration is a continuous
process with the rate dependent on the parameter (nutrients faster
than major cations and anions), the level (trace levels proportionately
faster than major levels) and the type of source. It is, of course,

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advisable to determine optimum storage conditions for particular sample

types encountered.

SELECTED REFERENCES

Brezonik, P.L., and G.F. Lee. 1966. Preservation of water
samples for inorganic nitrogen analysis with mercuric chloride.
Air Water Pollut. 10:549-53.

Hellwig, D.H.R. 1964. Preservation of water samples. Air Water
Pollut. 8:215-28.

Table 1. Guidelines for treatment and storage of samples.

Analysis	Storage conditions and duration prior to first manipulation		Initial manipulation	Storage conditions and allowable duration prior to analysis
Dissolved inorganic carbon	5 C	24 hours	Analysis	None
Dissolved organic carbon (manual)	5 C	48 hours	Filtration-chemical oxidation in ampoule	Room temp. Indefinitely
Dissolved organic carbon (automated)	5 C	24 hours	Filtration - Add $HgCl_2$	5 C 30 days
Particulate carbon and nitrogen	5 C	48 hours	Particulate collected on glass fiber filter	Filter @ -10 C. Indefinitely
Ammonia nitrogen	5 C	24 hours	Analysis	None
Nitrite nitrogen	5 C	24 hours	Filtration - analysis	None
Nitrate nitrogen	5 C	48 hours	Filtration - analysis	None
Total dissolved nitrogen	5 C	48 hours	Filtration - UV photo-combustion	5 C 5 days after UV
Soluble reactive phosphorus	5 C	24 hours	Filtration - analysis	None
Total dissolved phosphorus	5 C	48 hours	Filtration - UV photo-combustion	5 C 5 days after UV
Particulate phosphorus	5 C	48 hours	Particulate collected on glass fiber	Room temp. Indefinitely
Soluble reactive silicon	5 C	7 days	Analysis	None
Chloride	5 C	7 days	Filtration	5 C 30 days
Sulphate	5 C	7 days	Filtration	5 C 30 days
Sulphide	5 C	3 hours	Analysis	None
Ca, Fe, Mg, Mn, K, Na	5 C	7 days	Filtration - acidification	Room temp. - 30 days
Specific conductance	5 C	7 days	Analysis	None
Chlorophyll	5 C	48 hours	Particulate collected on glass fiber	-10 C in dark indefinitely
Dissolved oxygen	5 C	1 hour	Analysis	None
Methane	5 C	6 hours	Strip CH_4 from sample	1 week - sealed vial
Dissolved solids	5 C	7 days	Filtration	5 C 30 days
pH	5 C	24 hours	Analysis	None
Particulate solids	5 C	48 hours	Particulate collected on glass fiber	Dry, room temp. Indefinitely

METHOD PRECISION

We have obtained estimates of the precision attainable using the methods described in this manual, both for synthetic standards and natural water. Replicate samples (n=6) of synthetic standards and natural (Canadian Shield) water (six subsamples from a homogenized 10-liter sample) were analyzed in our routine laboratory. Standard deviation values (n=6) for natural water are given with each method and are compiled along with those for synthetic standards in Table II.

It should be emphasized that the precision data tabulated in Table II reflect method performance under routine conditions. With particular care many of these methods can be made to perform more precisely.

Errors for synthetic standards indicate the precision limits of method chemistry and instrumentation and have been termed Method Error (Table II). Errors for natural water include the additional errors arising from filtration and other manipulations, and are termed Laboratory Error.

We have not included estimates of errors involved in sampling a point source as these vary too greatly to permit generalization. Since sampling errors are often quite large (10-30% for particulate material) we cannot urge too strongly that persons involved in sampling obtain estimates of these errors before interpreting chemical data.

TABLE II. Some estimates of method precision for synthetic standards and Canadian Shield water. (Errors expressed as relative standard deviation n = 6)

Analysis	Synthetic Standards Level	Method Error (±)	Canadian Shield Water Level	Lab Error (±)
Dissolved inorganic carbon (manual)	1000 μmoles/l	<1%	300 μmoles/l	3%
Dissolved inorganic carbon (automated)	-	-	168 μmoles/l	2%
Dissolved organic carbon (manual)	1000 μmoles/l	2%	700 μmoles/l	2%
Dissolved organic carbon (automated)	-	-	600 μmoles/l	2%
Particulate carbon	200 μg/l	4%	1000 μg/l	3%
Dissolved methane	-	-	500 μmoles/l	3%
Ammonia - nitrogen (manual)	600 μg/l	2%	400 μg/l	1%
Ammonia - nitrogen (automated)	-	-	600 μg/l	2%
Nitrite - nitrogen (manual)	300 μg/l	1%	5 μg/l	10%
Nitrite - nitrogen (automated)	-	-	300 μg/l	<1%
Nitrate - nitrogen (manual)	300 μg/l	<1%	120 μg/l	3%
Nitrate - nitrogen (automated)	-	-	300 μg/l	<1%
Total dissolved nitrogen	-	-	640 μg/l	2%
Particulate - nitrogen	25 μg/l	5%	140 μg/l	4%
Soluble reactive phosphorus (manual)	100 μg/l	1%	-	-
Soluble reactive phosphorus (automated)	250 μg/l	<1%	-	-
Total dissolved phosphorus	-	-	20 μg/l	13%
Particulate phosphorus	150 μg/l	<1%	25 μg/l	6%
Silicon (manual)	10 mg/l	<1%	4.0 mg/l	2%
Silicon (automated)	1.00 mg/l	<1%	2.10 mg/l	<1%
Chloride (manual)	25 mg/l	3%	0.4 mg/l	21%
Chloride (automated)	10.0 mg/l	2%	-	-
Sulphate	25 mg/l	5%	5.0 mg/l	3%
Sulphate (automated)	10.0 mg/l	2%	-	-
Sulphide	-	-	330 mg/l	3%
Calcium	1.0 mg/l	<1%	2.5 mg/l	<1%
Iron	1.0 mg/l	3%	0.52 mg/l	6%
Magnesium	1.0 mg/l	1%	0.80 mg/l	2%

Table II (cont.) Some estimates of method precision for synthetic standards and Canadian Shield water. (Errors expressed as relative standard deviation n = 6).

Analysis	Synthetic Standards		Canadian Shield Water	
	Level	Method Error (±)	Level	Lab Error (±)
Manganese	1.0 mg/l	1%	-	-
Potassium	5.0 mg/l	3%	-	-
Potassium (low level)	-	-	0.33 mg/l	3%
Sodium	1.0 mg/l	2%	4.80 mg/l	<1%
Specific conductance	140 µS/cm	<1%	150 µS/cm	<1%
Chlorophyll	-	-	1.2 µg/l	12%
Dissolved oxygen	-	-	10.0 mg/l	2%
Dissolved solids	-	-	46 mg/l	9%
pH	8.50	<1%	-	-
Particulate solids	-	-	8 mg/l	6%

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DISSOLVED INORGANIC CARBON (TOTAL CARBON DIOXIDE)

PRECISION

    Level   - 300 μmoles CO_2/liter

    Standard deviation - $\pm$ 10 μmoles CO_2/liter

RANGE   - 10-2000 μmoles/liter total inorganic C

SAMPLE CONDITION
- Sample collected in a 50 ml polypropylene syringe or
- in a bottle which is filled completely, tightly sealed and stored at 5 C.
- Less than 24 hours old.
- Do not acidify, filter or freeze.
- Free from suspended carbonates.

METHOD PRINCIPLE
- A sample containing H_2CO_3[1], HCO_3^- and $CO_3^=$ is acidified (pH-4) converting carbonate and bicarbonate to H_2CO_3. Agitation of the sample with helium partitions gaseous CO_2 out of solution into the gas phase. The helium-CO_2 mixture (containing also N_2 and O_2) is then injected into a gas chromatograph for separation and detection of CO_2 by thermal conductance.

REAGENTS

    A. CO_2-free distilled water.

        Pass distilled water over a mixed bed resin to remove CO_2. Collect effluent without bubbling. Prepare fresh as needed.

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1. H_2CO_3 is used to represent all dissolved carbon dioxide (i.e. $CO_2+H_2CO_3$) following the convention of Garrels & Christ (Garrels, R.M. and Christ, C.L. 1965. Solution, Minerals and Equilibria. Harper & Row, N.Y.).

B.   Sulphuric acid - 1 N

Dilute 28 ml of concentrated H_2SO_4 to 1 liter with distilled water.

C.   Carbon dioxide standard

Dissolve 0.8401 g of dry $NaHCO_3$ in CO_2-free water.
Make to 1 liter with CO_2-free water without aeration.

1.00 ml = 10 µmoles CO_2
Prepare fresh daily.

D.   Carbon dioxide standard (alternate method)

Dilute "British Drug House" N/50 sodium carbonate
concentrates volumetric solution to volume specified
by manufacturer.

1.00 ml = 10 µmoles CO_2
Prepare fresh daily.

APPARATUS

A.   Fisher Hamilton gas partitioner Model 29 (or equivalent
equipment) set up as follows:

1. One 4-foot by 1/8" Poropak Q (80-100 mesh) chromato-
graphic column (Bypass loop in position of second column)

2. Sample loop valve - 2 ml volume.

3. Helium carrier gas flow 20-30 ml/min.

4. Detector current - 240 mA.

5. Detector signal to 10", 1 mV full-scale recorder - 0.2
inch per minute.

B.   "Cornwall" type dispensing syringe - 1 ml volume with
double female luer coupling.

C.   Disposable polypropylene syringe - 50 ml with caps.

D.   Plastic 3-way valves (6) with male and female couplings
(Ace Glass #5851-10).

E.   2 cylinders of helium with regulators or 1 cylinder of

helium with a stream splitting valve

Assemble apparatus as in Figure 2.

PROCEDURE

1. Using CO_2-free water to dilute the stock CO_2 standard, prepare a series of standards to cover the range of samples to be analyzed (50-2000 molar CO_2). See Note 1.

2. Push the plunger of a 50 ml plastic syringe all the way in to expel air from the syringe. Draw up 20 ml of blank, standard or sample into the syringe. For samples which are colledted in syringes expel liquid until 20 ml remains in the syringe and treat as for blanks and standards.

3. Inject 1 ml of 1 N H_2SO_4 into the syringe using the Cornwall dispensing syringe via the double female luer coupling.

4. Bring the syringe to the 3-way valve (K, Fig. 2) and inject helium at a slow rate (100 ml/min) into the syringe until the plunger is at the 50 ml mark. Remove the syringe and cap the tip.

    The syringe now contains:

    - 20 ml of blank, standard or sample
    - 1 ml of 1 N H_2SO_4
    - 29 ml of helium

5. Agitate the helium-liquid mixture vigorously for 10 seconds.

6. Inject 15 ml of the helium-CO_2 mixture from the syringe through valve (K, Fig. 2) and through the sample loop valve; then inject contents of sample loop onto the chromatographic column.

7. Disregard the first large peak (composite of N_2, O_2, and argon). Record the peak height and attenuation used for the second (CO_2) peak.

8. Treat blanks, standards and samples in identical fashion.

Note 1. The equilibrium partitioning of CO_2 between liquid and gas phases is temperature dependent. It is essential that samples and standards be analysed while at the same temperature.

(A) DETECTOR
(B) RECORDER
(C) CHROMATOGRAPHIC COLUMN
(D) DRYING TUBE
(E) SAMPLE LOOP VALVE
(F) SAMPLE LOOP
(G) HELIUM - CO_2 MIXTURE
(H) ACIDIFIED SAMPLE
(J) SYRINGE PLUNGER
(K) THREE-WAY VALVE

VENT
CARRIER GAS HELIUM
B
C
FISHER HAMILTON MODEL 29 GC.
D
VENT
E F
K
G
H
J
HELIUM FOR SAMPLE PROCESSING

APPARATUS FOR DETERMINATION OF INORGANIC CARBON
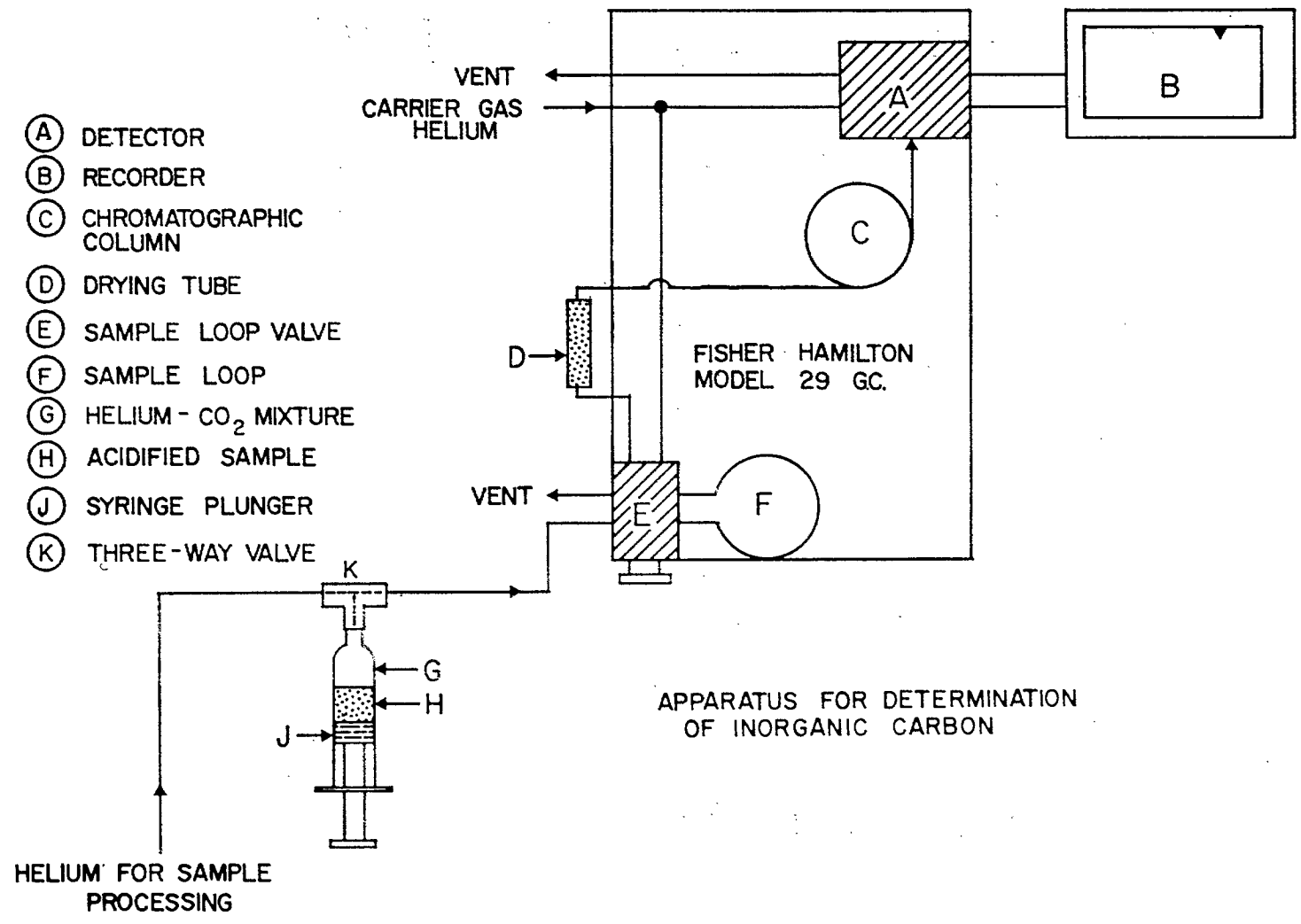
FIGURE 2.

CALCULATIONS

1. The scale factor for CO_2 can be calculated as follows:

    $$\text{Scale Factor } CO_2 = \frac{\text{Concentration } CO_2 \text{ (}\mu\text{moles/liter)}}{\text{Peak height (Std)} - \text{Peak height (Bl)}}$$

    Where peak height is (chart units) x (attenuation).

    This factor is constant up to 2000 μmoles and is approximately 3 μmoles/liter/chart unit for the instrument described.

2. Sample concentration is found by multiplying the observed peak height for the sample by the CO_2 scale factor.

3. The calculations above give a value for the total CO_2 content of the water sample. If pH and temperature values for the sample at the time of collection are available then (H_2CO_3), (HCO_3-), and $(CO_3^=)$ can be computed as described in section on Dissolved Carbonate System.

SELECTED REFERENCES

Stainton, M.P.   1973 . A syringe gas-stripping procedure for gas chromatographic determination of dissolved inorganic and organic carbon in fresh water and carbonates in sediments. J. Fish. Res. Board Can. 30:1441-1445.

DISSOLVED INORGANIC CARBON (AUTOMATED METHOD)

PRECISION

    Level   -   168 μmoles CO_2/liter

    Standard deviation   - $\pm$ 3 μmoles CO_2/liter

RANGE   -   10-800 μmoles CO_2/liter

SAMPLE CONDITION   -   See manual method for dissolved inorganic carbon

METHOD PRINCIPLE   -   This method employs the same automated conductimetric technique used for measurement of dissolved organic carbon. The important difference is the manner in which samples are sealed in plastic sample cups to prevent contact with atmosphere prior to analysis. For details of CO_2 detector see automated dissolved organic carbon method. A manuscript (M.P. Stainton) describing this method is in preparation.

REAGENTS

    A. CO_2-free distilled water.

         See automated organic carbon method.

    B.   Acid persulphate.

         See automated organic carbon method.

    C.   Barium hydroxide stock - 0.02 N.

         See automated organic carbon method.

    D.   Barium hydroxide working solution - 0.001 N.

         See automated organic carbon method.

E.   Ascarite - 30-60 mesh.

F.   Helium - Low purity with 2-stage regulator.

G.   Wash water.

     See automated organic carbon method.

H.   Carbon standard.

     See dissolved inorganic carbon (manual method).

APPARATUS

A.   Sampler - Carlo Erba or equivalent instrument having a pickup probe alternating between sample and a wash water reservoir, variable "sample" and "wash" cycle times and capable of utilizing Technicon[R], 10 ml sample cups. The Carlo Erba sampler was modified to include a helium bubbler in the wash water reservoir (to maintain a low CO_2 blank) and a sharpened pickup capillary to puncture the tape seal on the cups. See Figure 3.

Sample time	1.2 minutes
Wash time	1.7 minutes
Sampling rate	20 per hour

B.   Sample cups - 10 ml (contains 9.5 ml)

     Technicon Part No. 127-0080P01

C.   Scotch "Magic Tape" [TM] - This is the only tape found to give satisfactory seal and yet not stick to the pickup probe.

D.   Proportioning pump - 8 channels required.

E.   Flow-through conductivity cell

     Radiometer #CDC 314
     Cell constant = 0.316 cm^{-1}

F.   Conductivity meter

     Radiometer CDM 3 - 1500µS full scale

WASH WATER

| HELIUM

↓ · ↓ SAMPLE

DRAIN

WASH WATER
RESERVOIR

SAMPLE PICKUP

SAMPLE CUP (9ml)

SAMPLE TRAY FOR
40 SAMPLES
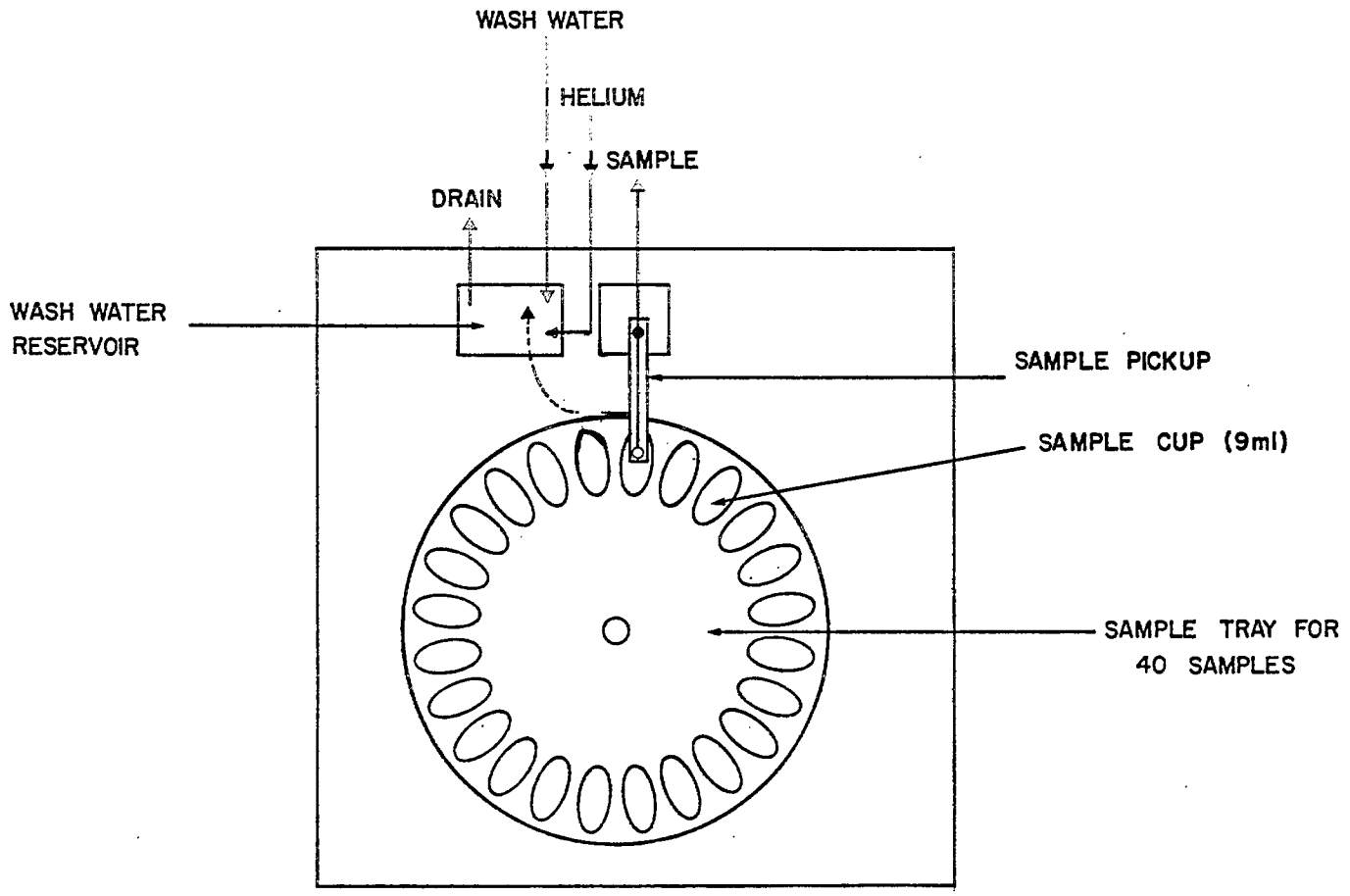
SAMPLER   TOP VEIW

FIGURE 3

29
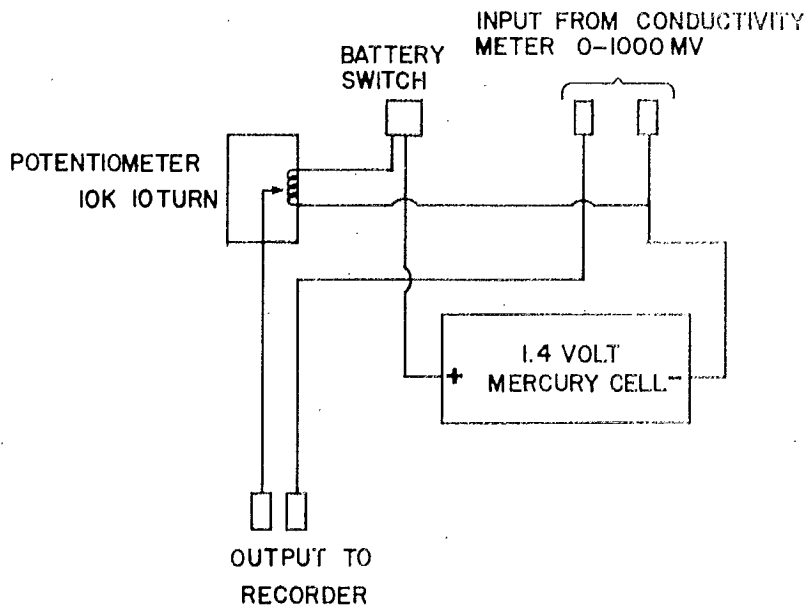
BASELINE OFFSET INTERFACE

FIGURE 4

G.   Baseline offset interface - The signal output from the
     conductivity meter is 0 to -1000 mV full scale. The
     baseline signal produced by 0.001 N $Ba(OH)_2$ is about
     -200 mV. Since voltage variation produced by dissolved
     CO_2 is small, the initial baseline signal must be offset
     by a +200 mV source. The interface unit diagrammed in
     Figure 4 provides a variable voltage to offset the
     baseline. The remaining DIC signal can then be amplified
     in the recorder.

H.   Strip chart recorder.

        100 mV full scale - 0.2 inch per minute.

I.   Ascarite column - 10 cm x 2 cm (A CO_2 trap).

J.   Gas-liquid phase separator - See Figure 5.

K.   Temperature stabilizing bath to house conductivity cell
     and mixing coils. See Figure 6.

PROCEDURE

1.   With the apparatus assembled as in Figure 7; turn on the
     proportioning pump, the helium flow to the wash water
     reservoir on the sampler, the conductivity meter, and the
     recorder and allow the system to equilibrate for 20
     minutes. Zero recorder.

2.   Sample cups are sealed with 2-inch lengths of Scotch brand
     "Magic Tape". The tape is thoroughly sealed to the lip of
     the cups by pressing the lip covered with tape onto a
     slightly compressible surface such as a pad of paper. A
     perfectly flat seal is essential and is quite easy to
     obtain. In some instances the plastic cups have a small
     burr on them which will cut the tape. This must be removed,
     usually with a finger nail. Cups can be reused following
     removal of old tape, washing, drying and application of
     new tape.

3.   Sample cups sealed with a 2-inch strip of tape are placed
     on the sample wheel. A small amount of tape overlaps from
     each cup and effectively bonds all of the cups to each
     other on the sample wheel.

4.   Sample is either collected in a 50 ml plastic syringe or
     transferred to a syringe from its sample bottle. Sample

GAS

POLYETHYLENE
T CONNECTOR
7mm I.D.

TYGON TUBING
3mm O.D. 1.5mm I.D.

TYGON TUBING
7mm O.D. 3mm I.D.

GAS + LIQUID

15 mm

TYGON TUBING
7mm O.D. 5.5mm I.D.

TYGON TUBING
5.5mm O.D. 4mm I.D.

LIQUID + GAS
TO WASTE

GAS-LIQUID PHASE SEPARATOR

FIGURE 5

TEMP. SENSOR

HOLES DRILLED
FROM BOTTOM

COIL

HEATING ELEMENT

CONDUCTIVITY
CELL

COIL

TEFLON PLUGS

UNIT IS COMPLETELY
ENCLOSED BY A BLOCK
OF STYRAFOAM.

ALUMINUM BLOCK

TECHNICON MIXING COIL
(MODIFIED AS SHOWN)

CONDUCTIVITY CELL
(RADIOMETER TYPE
CDC 314 MODIFIED
AS SHOWN)

OIL

TEMPERATURE
SENSOR

HEATING ELEMENT

ELECTRONIC
TEMPERATURE
CONTROLLER

SPACE AROUND HEATING
ELEMENT AND TEMP.
SENSOR FILLED WITH
THERMAL COMPOUND
(SPACE SHOULD BE
KEPT TO A MINIMUM)

CONTROLLED TEMPERATURE HEATING BLOCK

FIGURE 6

MANIFOLD FOR DISSOLVED INORGANIC AND ORGANIC CARBON

FIGURE 7

is injected into the sealed sample cups using an 18 G
1 1/2 inch needle. The needle is inserted through the
tape seal at the outside edge of the cup (as it sits on
the sample wheel). This is a high point in the sloping
surface of the 10 ml cup so that as liquid is injected
into the cups all of the air within the cup escapes
leaving no bubbles on the underside of the tape.

5. Using CO_2 free distilled water prepare standards appropriate
   for the concentration range of samples anticipated.

6. Place blanks, standards and samples on the sample wheel as
   described above and start the sampler.

7. Record peak height of blanks, standards and samples

CALCULATIONS

1. From peak height values of standards obtain a scale factor
   F where

$$F = \frac{\text{Standard concentration } (\mu\text{moles } CO_2/\text{liter})}{\text{Peak height standard} - \text{Peak height blank}}$$

2. Multiply peak height of samples by scale factor F to
   obtain μmoles inorganic carbon per liter.

DISSOLVED ORGANIC CARBON

PRECISION

    Level   - 700 μmoles C/liter

    Standard deviation   - ± 16 μmoles C/liter

OPERATING RANGE   - 50-2000 μmoles dissolved organic carbon per liter.

SAMPLE CONDITION   - Filtered through ignited Whatman GF/C and stored at 5 C.
                                - Less than 48 hours old.

METHOD PRINCIPLE   - If a water sample is acidified (below pH 4) and bubbled vigorously with helium, the inorganic carbon can be removed. The remaining carbon is considered to be dissolved organic carbon (DOC). If the acidified sample is then treated with potassium persulphate at elevated temperature and pressure, organic carbon compounds are fragmented and oxidized to CO_2. The reaction is carried out in sealed ampoules which are autoclaved at 121 C for 1 hour.

                           The CO_2 produced is measured as for inorganic carbon and is a measure of the organic carbon content of the sample.

REAGENTS

    A.   Low-carbon water - Effluent from Millipore "Super Q" system.

    B.   Potassium persulphate - Analytical reagent grade $K_2S_2O_8$.

    C.   Perchloric acid - Sp. Gr. - 1.70.

MANIFOLD SIZE
INCREASED BY
ADDING
ON VALVES

GANG VALVE

HELIUM

TYGON TUBING

20 GAUGE -6" NEEDLE

SAMPLE
LIQUID

25 ml
AMPOULE
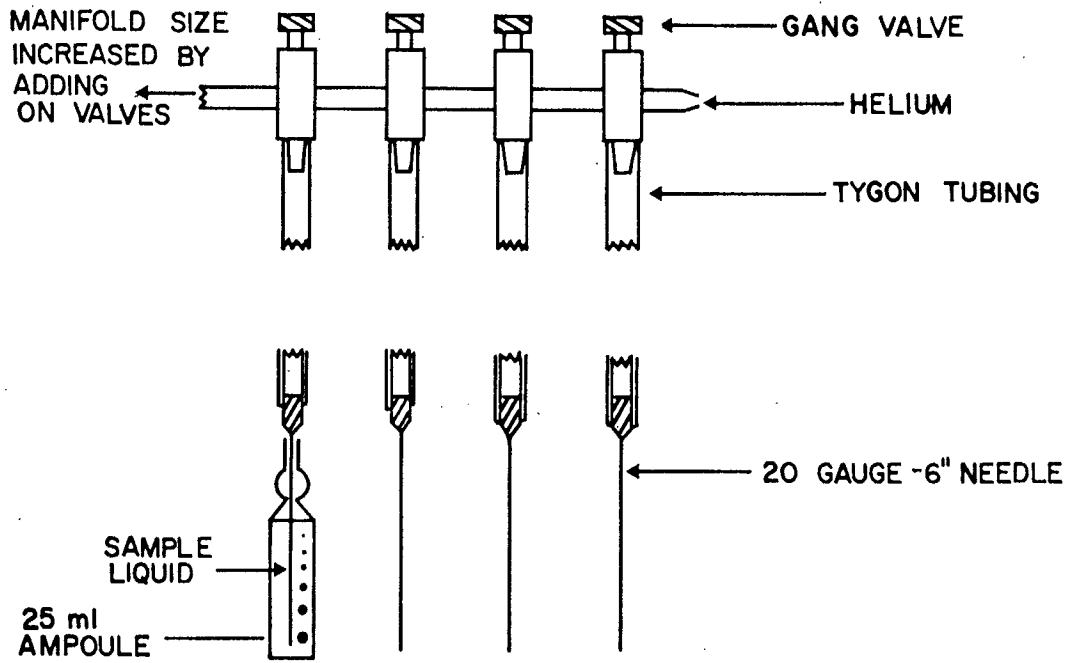
Inorganic Carbon Stripping Manifold

Figure 8.

7.   Bubble sample for 20 minutes to drive off inorganic carbon.

8.   Quickly seal the ampoule with the oxy-propane torch taking care not to entrap combustion gases from the flame in the ampoule. A rounded bubble seal is desirable for strength.

9.   Autoclave samples at 121 C for 1 hour.

      Ampoules may be stored indefinitely after this is done.

10.   An autoclaved sample is cooled to room temperature and opened. 20 ml of the ampoule contents are transferred to a 50 ml plastic syringe through a wide-bore cannula. It is important to carry out this transfer quickly but without degassing the sample which results if the syringe plunger is pulled out too fast.

11.   The sample on the 50 ml syringe is analyzed as for inorganic carbon.

12.   Obtain peak height (chart units x attenuation) values for low-carbon water, glucose standards, and samples.

CALCULATIONS

1.   A scale factor for the gas chromatograph can be calculated as follows:

$$\text{Scale Factor (Organic C)} = \frac{\text{Glucose-C concentration (}\mu\text{moles/liter)}}{\text{Peak height (Std)} - \text{Peak height (Bl)}}$$

where peak height = (Chart Units) x (Attenuation).

2.   Sample concentration is found by multiplying observed peak height for the sample by the scale factor. Reagent blank is usually negligible.

3.   Dilution calculations

      Organic carbon concentration in samples requiring dilution with low carbon water can be calculated using the equation below. Organic carbon content of dilution water must be determined.

D.   Glucose – organic carbon standard.

Dissolve 0.3003 g of glucose in low-carbon water and make to 1 liter. Store at 5 C. Discard if a precipitate develops.

1.00 ml = 10 µmoles glucose-C

APPARATUS

A.   Inorganic carbon stripping manifold as in Figure 8, assembled from 20 gauge, 6 inch, stainless steel needles, tygon tubing and ganged aquarium valves.

B.   Helium cylinder and regulator.

C.   Glass ampoules – pre-scored necks to contain 25 ml.

D.   Oxy-propane torch to seal ampoules.

E.   Metal racks for ampoules.

F.   Muffle furnace to pre-ignite ampoules.

G.   Autoclave with slow exhaust cycle.

PROCEDURE

1.   Pre-ignite (550 C for 8 hours) enough ampoules for the samples to be analyzed.

2.   Place 0.1 g (approximately) of potassium persulphate in each ampoule.

3.   Prepare a series of glucose standards to cover the range of the samples to be analyzed (50-2000 µmoles C).

4.   Place 25 ml of blank, standard, or filtered sample into an ampoule containing potassium persulphate.

5.   Add 0.1 ml of perchloric acid to the ampoule.

6.   Insert one of the stainless steel needles of the CO_2 stripping manifold into the ampoule and turn on the helium.

$$C_1 = (C_2 \times D) - (C_3 \times (D-1)$$

where

C_1 = conc. of organic carbon in sample.
C_2 = conc. of organic carbon in diluted sample.
C_3 = conc. of organic carbon in dilution water.
D = dilution factor.

SELECTED REFERENCES

Menzel, D.W., and R.F. Vaccaro. 1964 . The measurement of dissolved organic and particulate carbon in sea water. Limnol. Oceanogr. 138-142.

Stainton, M.P. 1973 . A syringe gas stripping procedure for gas chromatographic determination of dissolved inorganic and organic carbon in fresh water and carbonates in sediments. J. Fish. Res. Board Can. 30:1441-1445.

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DISSOLVED ORGANIC CARBON (AUTOMATED METHOD)

PRECISION

    Level   - 600 µmoles C/liter

    Standard deviation   - ±10 µmoles C/liter

OPERATING RANGE   - 10-800 µmoles C/liter

SAMPLE CONDITION   - Filtered through Whatman GF/C.
                             - Stored at 5 C.
                             - Less than 48 hours old.

METHOD PRINCIPLE   - Under appropriate reaction conditions (pH 2 and adequate oxygen supply) organic carbon compounds can be photo-oxidized to CO_2 by exposure to high intensity short U.V. radiation. Reaction rate is fast enough to achieve complete breakdown using a continuous flow system. The samples are acidified and bubbled with helium prior to analysis to remove dissolved inorganic carbon. The CO_2 produced by photocombustion is measured using an automated conductimetric technique. CO_2 is sparged from the liquid phase with CO_2-free air. The air-CO_2 mixture is bubbled into a stream of barium hydroxide where CO_2 is absorbed and precipitated as barium carbonate. The barium hydroxide solution is then pumped through a flow-through conductivity cell. Conductance of the barium hydroxide solution is inversely related to the level of organic carbon present in the sample. A manuscript (M.P. Stainton) describing this method is in preparation.

REAGENTS

    A.   "Zero" carbon water.

        See Note 1 at end of method.

    B.   Acid persulphate.

        Dissolve 5 g of reagent grade potassium persulphate in 1 liter of distilled deionized water.

        Add 1 ml of high purity concentrated sulphuric acid. Ultre: (J.T. Baker) and "Aristar" (B.D.H.) brands have acceptable carbon levels.

    C.   Barium hydroxide stock - 0.02 N.

        Dissolve 3.2 g of $Ba(OH)_2.8H_2O$ in 1 liter of distilled and deionized water (store in glass and seal with a rubber stopper).

    D.   Barium hydroxide - working solution - .001 N.

        Dilute 100 ml of stock barium hydroxide to 2 liters with distilled and deionized water (store in glass and seal with a rubber stopper).

    E.   Ascarite or Colorcarb (Perkin Elmer Part No. 240-0115) - 30-60 mesh.

    F.   Wash water.

        Use "Zero carbon" water (reagent A).

    G.   Organic carbon standard - stock.

        Dissolve 0.601 g of reagent grade urea in 1.00 liter of distilled and deionized water. Store in stoppered glass container at 5 C.

                1.00 ml = 10 μmoles carbon

APPARATUS

A. Sampler - Carlo Erba - Sample probe modified to alternate
    between sample and wash water, and to bubble acidified
    samples with helium. See Figure 9.

    Sample time   - 1.2 minutes
    Wash time   - 1.7 minutes
    Sample rate   - 20 per hour

B. Proportioning pump - 8 channels required.

C. Continuous flow, short U.V. photo-oxidizer. See Figure 10.

    Apparatus consists of:

    1. 700 watt Westinghouse mercury vapor lamp and ballast.

    2. Quartz coil; 32 turns of 4 mm O.D. 2 mm I.D. quartz
        tubing. Coil diameter 7 cm. Coil internal volume $\simeq$
        20 ml.

    3. Quartz jacket tube to protect lamp from cooling
        effect of fans.

    4. Exhaust fans to cool coil.

    5. Support assembly to hold lamp, fans, and quartz coil
        in correct alignment.

D. Flow-through conductivity cell.

    Radiometer CDC314 - Cell constant = 0.316 cm^{-1}.

E. Conductivity meter.

    Radiometer CDM 3 - 1500 μS full scale.

F. Baseline offset interface. The signal output from the
    conductivity meter is 0 to -1000 mV. The baseline signal
    produced by 0.001 N $Ba(OH)_2$ is about -200 mV. Since
    voltage change produced by DOC is small the initial base-
    line signal must be offset by a +200 mV source. The
    interface diagrammed in Figure 11 provides a variable
    voltage to offset the baseline. The remaining DOC signal
    is then amplified by the recorder.

G. Strip chart recorder.

    100 mV full scale - 0.2 inch per minute.

WASH WATER

HELIUM

SAMPLE

DRAIN

WASH WATER
RESERVOIR

SAMPLE PICKUP AND
SPARGING PROBES

SAMPLE CUP (9ml)

SAMPLE TRAY FOR
40 SAMPLES

SAMPLER TOP VEIW

FIGURE 9

CONTINUOUS FLOW U.V. DIGESTOR

FIGURE 10

BATTERY SWITCH

INPUT FROM CONDUCTIVITY
METER 0–1000 MV

POTENTIOMETER
10K 10 TURN

1.4 VOLT
+ MERCURY CELL −

OUTPUT TO
RECORDER
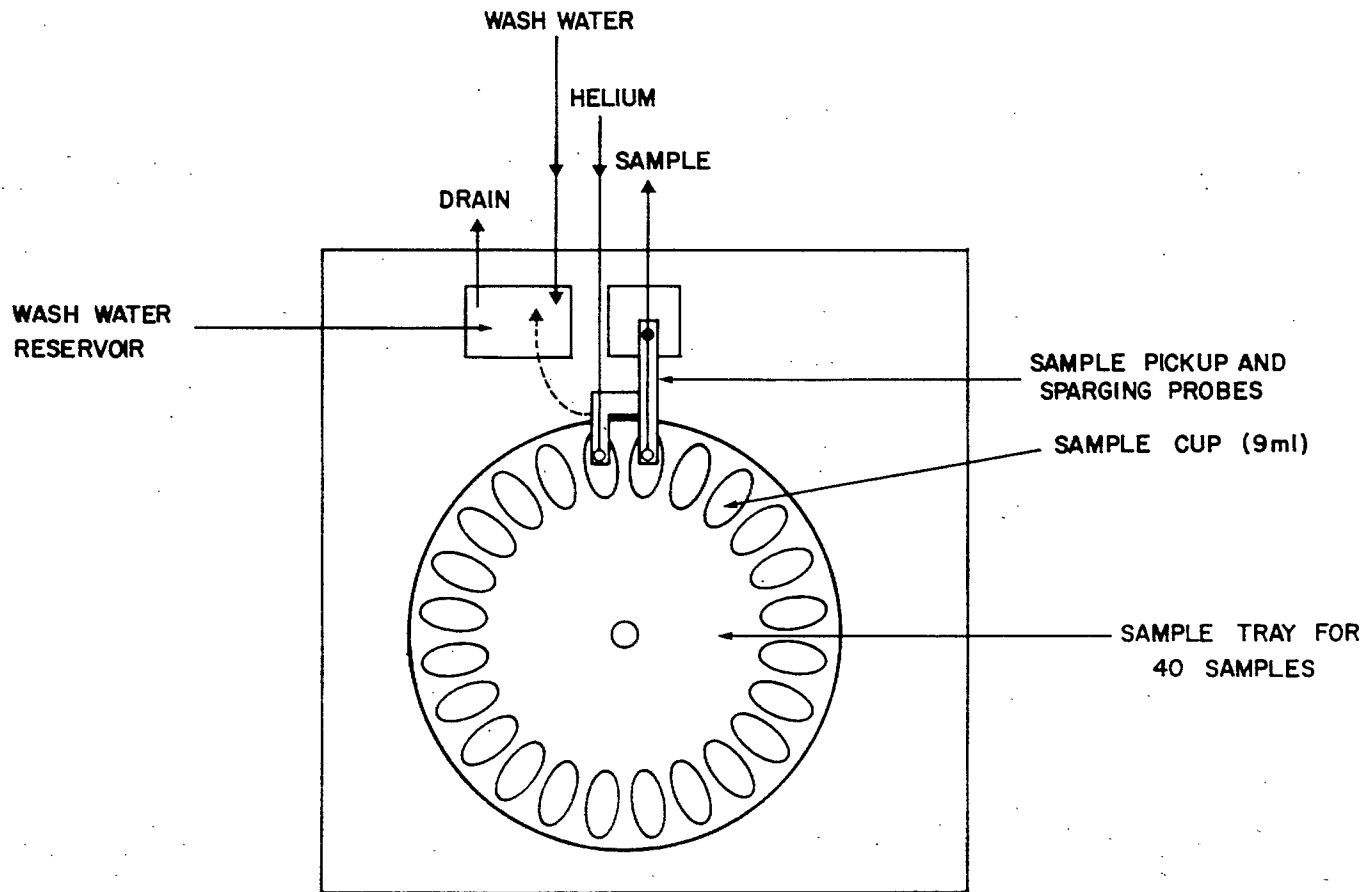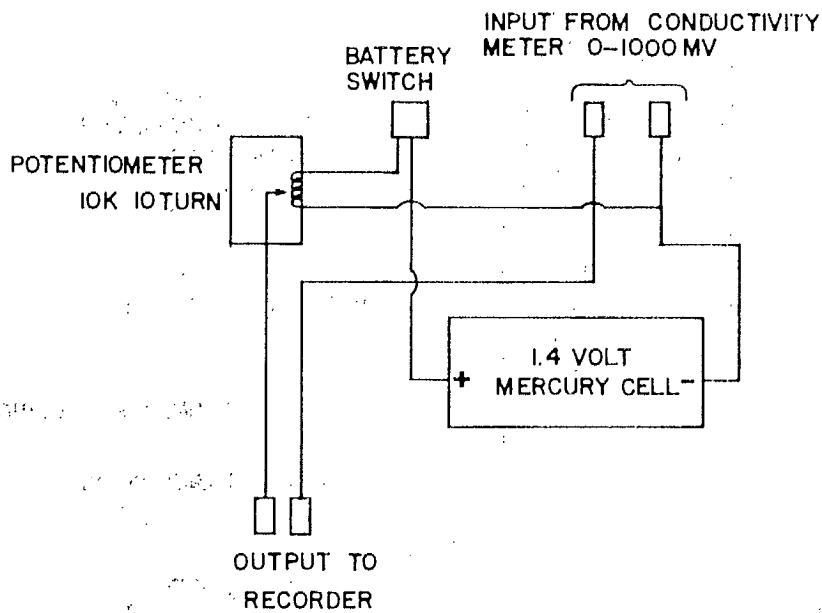
BASELINE OFFSET INTERFACE

FIGURE 11

H.   Ascarite column - 10 cm x 2 cm.

I.   Gas-liquid phase separator - Figure 12.

J.   Constant temperature housing for conductivity cell and mixing coils. See Figure 13.

K.   Helium - Low purity with 2 stage regulator.

PROCEDURE

1.   With the apparatus assembled as in Figure 14, turn on pump and helium flow (50 ml/min).

2.   When liquid has filled the system, turn on conductivity meter and recorder and allow systems to equilibrate for 20 minutes. Zero recorder.

3.   Turn the fans of the photo-oxidizer on, then the lamp.

4.   Prepare urea standards from stock solution and distilled and deionized water to cover the range of samples to be analyzed.

5.   Acidify blanks, samples and standards by adding 100 μl of concentrated H_2SO_4 per 100 ml.

6.   Add blanks, standards and samples to sampler and start sampler.

7.   Reject the first peak recorded as the first sample on the wheel receives no helium bubbling.

8.   Record peak height of blanks, standards and samples.

9.   For samples exceeding 800 μmoles C/liter, dilute with distilled and deionized water before analysis and determine carbon blank of dilution water.

GAS

↑

TYGON TUBING
3mm O.D. 1.5mm I.D.

TYGON TUBING
7mm O.D. 3mm I.D.

POLYETHYLENE
T CONNECTOR
7mm I.D.

GAS + LIQUID ——————→

15 mm

TYGON TUBING
7mm O.D. 5.5mm I.D.

TYGON TUBING
5.5mm O.D. 4mm I.D.

↓

LIQUID + GAS
TO WASTE

GAS-LIQUID PHASE SEPARATOR

FIGURE 12

CONTROLLED TEMPERATURE HEATING BLOCK

FIGURE 13

ATMOSPHERE

ASCARITE

ATMOSPHERE (CO₂ FREE)

1.00 ml/MIN

DIGESTOR BYPASS

ATMOSPHERE (CO₂ FREE)

2.90 ml/MIN

Ba (OH)₂
(0.001 N)

3.40 ml/MIN

2.00 ml/MIN

SAMPLE
ACIDIFIED (pH2)
INORGANIC CARBON FREE

2.00 ml/MIN

VALVE A

VALVE B

SHORT MIXING COIL

SHORT MIXING COIL

PHASE SEPERATORS

GAS WASTE

0.60 ml/MIN

U.V. DIGESTOR

WASTE

CONDUCTIVITY CELL

1.60 ml/MIN

SULPHURIC ACID (0.4N)
POTASSIUM PERSULPHATE (5g/L)

DENOTES A PUMPED GAS
OR LIQUID FLOW AT THE
RATE INDICATED

DOTTED LINE DENOTES PART OF
APPARATUS MAINTAINED AT 35C

RECORDER

BASELINE OFFSET
INTERFACE

CONDUCTIVITY
METER

FIGURE 14

MANIFOLD FOR DISSOLVED INORGANIC AND ORGANIC CARBON

CALCULATIONS

1. From peak height values of standards obtain a scale
   factor F where

   $$F = \frac{\text{Standard concentration (}\mu\text{moles C/liter)}}{\text{Peak height standard}}$$

2. Multiply peak height of samples by scale factor F to
   obtain μmoles organic carbon per liter.

3. If samples are diluted before analysis then

   $$C_1 = (C_2 \times D) - (C_3 \times (D-1))$$

   Where

   C_1 = conc. of DOC in sample
   C_2 = conc. of DOC in diluted sample
   C_3 = conc. of DOC in dilution water
   D = dilution factor

NOTE 1

Zero carbon water is prepared by introducing acidified (1 ml
H_2SO_4 per liter) distilled deionized water into the manifold of
figure via the sample pump tube. The distilled water is photo-
cumbusted and collected immediately after leaving the U.V.
digestor. Digested effluent contains inorganic carbon which can
be removed by bubbling with helium. It is convenient to prepare
this water in the evening when the analytical system is not being
used. In a normal evening 3 liters of zero carbon water can be
prepared which is more than enough for a day's analyses.

NOTE 2

The 700-watt mercury vapour lamp recommended (Part No. H35NA-700/C)
is supplied with the arc tube sealed in a glass envelope which
must be removed to gain access to the short UV. The envelope is
removed by filing a nick in the globe 5 cm from the metal base.
By placing a red hot 2 mm diameter glass rod a few mm from the
scratch a crack will develop. Repeated treatment with the hot
glass rod will extend the crack around the circumference of the
globe which can then be removed.

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DISSOLVED CARBONATE SYSTEM

The equilibrium levels of the various components of the carbonate system depend on temperature, pH, ionic strength and dissolved inorganic carbon levels. Measurement of these permits computation of the levels of H_2CO_3, $CO_3^=$, and HCO_3^- in the original sample (if pH and temperature measurements are taken upon sampling).

The carbonate equilibrium system involves the following chemical reactions:

1. $CO_2 + H_2O \rightleftharpoons H_2CO_3$

2. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
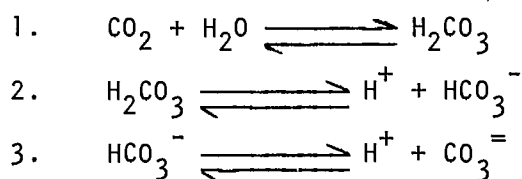
3. $HCO_3^- \rightleftharpoons H^+ + CO_3^=$

The equilibrium constants for these reactions are:

1. $Kc = \dfrac{[H_2CO_3]}{P_{CO_2}} = 10^{-[1.13 + (0.0131 \times T)]}$

where P_{CO_2} = the partial pressure of CO_2 in the atmosphere $\equiv 10^{-3.5}$ atm.

2. $Ka = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-(6.57 - (0.00926 \times T))}$

3. $Kb = \dfrac{[H^+][CO_3^=]}{[HCO_3^-]} = 10^{-(10.614 - (0.0117 \times T))}$

In all these equations T is the temperature (Celsius) of the water sample at the time of collection. It should also be noted that the values given for the constants only apply to waters with a low ionic strength.

To calculate the concentrations of the various components of the system the following equations are used:

A. $$[H_2CO_3] = \frac{[H^+]^2 \times \Sigma CO_2}{[H^+]^2 + ([H^+] \times Ka) + KaKb}$$

where $\Sigma CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^=] =$ dissolved inorganic carbon
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (moles/liter)

B. $$[HCO_3^-] = \frac{[H^+] \times Ka \times \Sigma CO_2}{[H^+]^2 + [H^+] Ka + KaKb}$$

C. $$[CO_3^=] = \frac{KaKb \times \Sigma CO_2}{[H^+]^2 + [H^+] Ka + KaKb}$$

H^+ is calculated from the pH of the sample measured at the time of collection. $H^+ = 10^{-pH}$.

SELECTED REFERENCE

Garrels, R.M., and C.L. Christ. 1965. Solutions, Minerals and Equilibria. Harper & Row, N.Y. 450 p.

PARTICULATE CARBON AND NITROGEN

PRECISION

Nitrogen	Level	-	140 µg N/liter
	Standard deviation	-	± 6 µg N/liter
Carbon	Level	-	1000 µg C/liter
	Standard deviation	-	± 30 µg C/liter

OPERATING RANGE
- 0.1-100 µg N or 1-500 µg C per filter paper. Operating range in terms of water samples depends on the volume available or possible to filter.

SAMPLE CONDITION
- Water sample stored at 5 C.
- Less than 48 hours old.
- Particulate collected on a pre-ignited glass fiber filter paper.
- Filter paper with particulate, vacuum desiccated in the dark to dryness.
- Dry filter papers stored in individual plastic petri dishes at -10 C for an indefinite period.

METHOD PRINCIPLE
- Particulate material on a glass fiber filter paper is combusted in an oxygen helium atmosphere at 700 C. The combustion products are then swept by helium carrier gas over a heated copper oxide-silver vanadate bed where they are oxidized to CO_2, H_2O, and oxides of nitrogen. The gas stream then passes over hot copper where oxides of nitrogen are reduced to N_2 and excess O_2 is removed. The remaining CO_2, H_2O, and N_2 in the

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helium carrier are then measured differently depending on the instrument used.

In the Carlo Erba Model 1102, a dynamic, continuous flow, CHN analyzer, the three gases are separated chromatographically and analyzed with a single thermal conductance detector. (See Hauser 1973 for details of operation.)

In the Perkin Elmer Model 240, a stop-flow type CHN analyzer, the gas mixture is introduced into a reservoir where CO_2, H_2O, N_2, and He are mixed. The gas mixture is then diverted through a series of columns which sequentially remove H_2O and CO_2. Each of these columns is bracketed by a pair of thermal conductance detectors, the difference between their signal outputs being proportional to the amount of H_2O or CO_2 removed in the column (see Figure).

The final gas stream containing N_2 and helium goes through a detector whose signal output when referred to pure helium, is proportional to N concentration.

REAGENTS

Acetanilide — Calibration standard for both CHN analyzers (e.g. NBS standard #141B)

Carbon   71.09%
Nitrogen 10.36%
Hydrogen 6.71%

The following are required to construct combustion and reduction tubes, traps for CO_2 and H_2O, and for instrument operation. See instrument

manuals for specifics of column construction.

PE 240	- Copper oxide
	- Copper metal (60-100 mesh)
	- Silver vanadate
	- Magnesium perchlorate
	- Colorcarb
	- Helium 99.995 mole %
	- Oxygen 99.995 mole %
Carlo Erba 1102	- Copper oxide
	- Copper metal (60-100 mesh)
	- Silver vanadate
	- Magnesium perchlorate
	- Helium - low purity
	- Oxygen - 99.5%
	- Compressed air
	- MnO_2 catalyst-ignited 16 hours @ 550 C.

APPARATUS

1. Perkin Elmer Model 240 Elemental Analyzer as in Figure 15.

- A slight modification to manufacturer's ladles was made to facilitate handling of filter papers.
- Cycle time is about 14 minutes to obtain both C and N values.

or

2. Carlo Erba Model 1102 Elemental Analyzer.

- Considerable modification has been made to the arrangement of combustion tubes and gas flows (Hauser 1973).
- Cycle time is about 7 minutes to obtain both C and N values.

3. Cahn Gram Electrobalance.

- Model G or equivalent, to weigh to nearest µg.
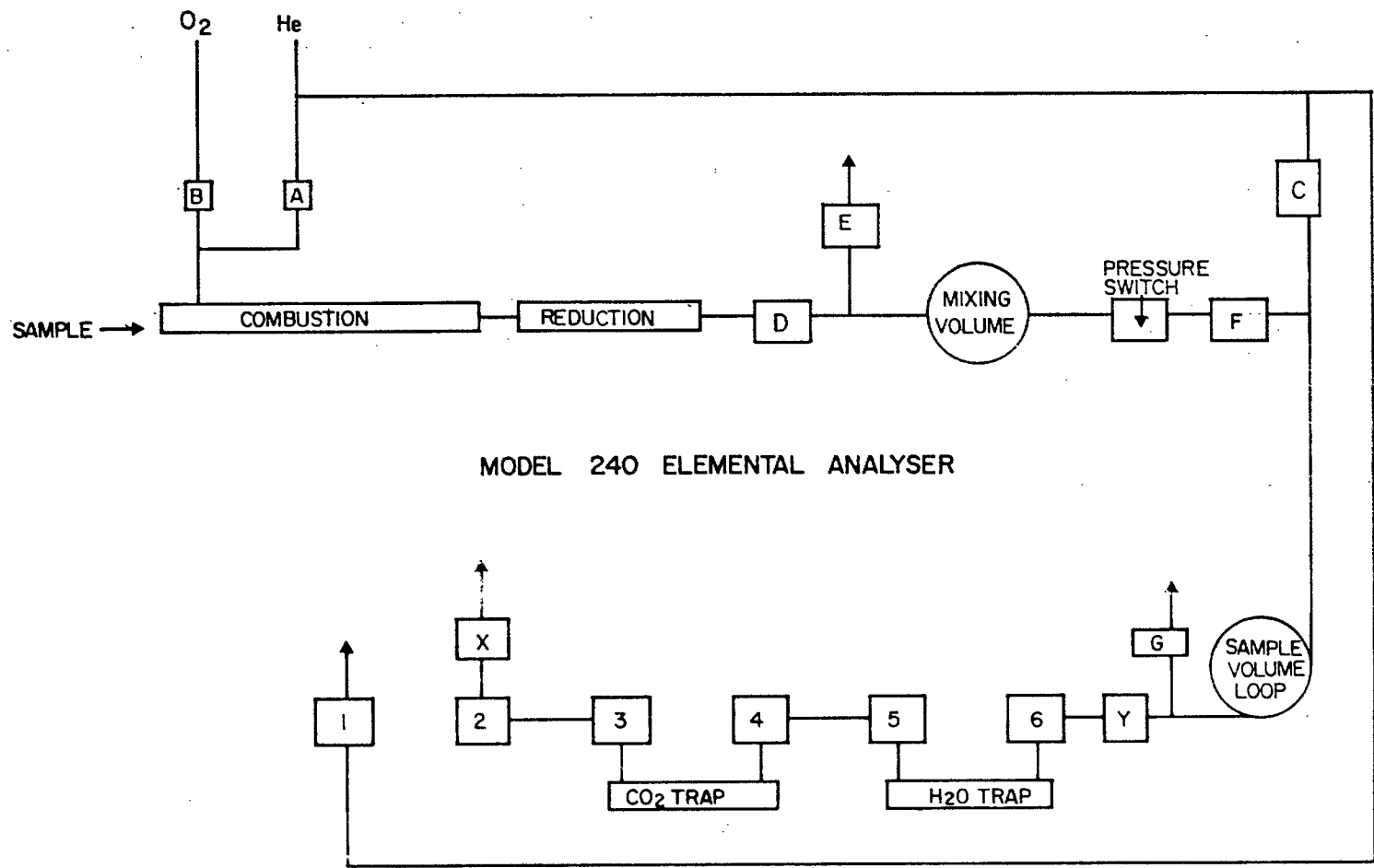
MODEL 240 ELEMENTAL ANALYSER

FIGURE 15.

A - G	SOLENOID CONTROL VALVES	I - 2	NITROGEN DETECTORS
X - Y	SAFETY SENSORS	3 - 4	CARBON DECTECTORS
		5 - 6	HYDROGEN DETECTORS

PROCEDURE

SAMPLE PREPARATION

1. Ignite Whatman 4.25 cm GF/C glass fiber filter papers at
    550 C for 16 hours. Store in dust-free container and
    handle only with forceps.

2. To filter a sample:

    A. Agitate the sample bottle and quickly pour the
        required volume V (usually 100 ml) into a graduated
        cylinder.

    B. Pour the sample onto a filter paper held in a Millipore
        47 mm filtration assembly.

    C. Filter at 15 inches Hg vacuum just to dryness then
        break vacuum.

3. Place the damp paper in a vacuum desiccator in the dark
    over night.

4. Place the dry sample, face up, in a labelled,plastic,
    covered petri dish (50 mm diam.) and place in a freezer at
    -10 C.

INSTRUMENTAL ANALYSIS

The following is a general outline of the procedure followed.
The procedure below should be followed only when the analyst is
thoroughly familiar with the complexities of the instruments described.

1. Samples of acetanilide standard from 0.1-0.4 mg are
    weighed in platinum boats to the nearest µg.

2. With the instrument ready to operate (see manual for
    machine settings) an acetanilide standard, ignited filter
    paper blank or ignited filter paper with sample is placed
    in a ladle.

3. The ladle is then placed in a cool zone of the instrument's
    combustion tube and atmospheric contaminants purged for
    2-3 minutes with helium.

4. The ladle is then injected into the hot zone of the
    combustion tube where ladle contents are combusted.

5. Chart units and attenuation for C and N signals are recorded.

CALCULATIONS

1. Scale factors for nitrogen and carbon are calculated as follows:

$$\text{Scale Factor (C or N)} = \frac{\mu g \text{ C or N per ladle}}{\text{Peak height } (C \text{ or } N)}$$

where Peak height = (chart units) x (attenuation)

2. Peak heights for samples are corrected for blank paper values and multiplied by the C and N scale factors above to give μg C and N per sample (on the filter).

3. The μg C and N per filter paper values obtained above are multiplied by the volume factor to give the suspended N and C concentration in the original water sample.

i.e. μg C or N/paper x $(\frac{1000}{V})$ = μg/liter C or N in the water sample

where V is the volume filtered in mls.

SELECTED REFERENCES

Hauser, B.W. 1973 Modifications to Carlo Erba elemental analyzer for rapid determination of carbon and nitrogen in suspended matter of natural water. Fish. Res. Board Can. Tech. Rep. 412: p.

Stockner, J.G., and F.A.J. Armstrong. 1971 Periphyton of the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Board Can. 28:215-229.

DISSOLVED METHANE

PRECISION

Level	-	500 μmoles CH_4/liter
Standard deviation	-	±13 μmoles CH_4/liter

OPERATING RANGE

- 0.1-5000 μmoles CH_4/liter

SAMPLE CONDITION

- Sampling technique is critical for this method - <u>see section on sampling methods</u>.
- If methane oxidation is likely, the sample should be preserved immediately upon collection by adding NaOH to increase pH to 11.
- Methane should be stripped from the sample within 6 hours of collection.
- Stripped gases may be held in serum vials for at least one week prior to analysis.

METHOD PRINCIPLE

- Sample containing methane is placed in a syringe along with methane-free nitrogen. Agitation of the syringe partitions methane out of liquid into the gas phase. The gas phase is then injected into a water-filled serum vial by displacement of water from the vial. An aliquot of the nitrogen-methane mixture is then injected into a gas chromatograph equipped with a flame ionization detector.

REAGENTS

A. Sodium hydroxide

Dissolve 0.8 g NaOH in 50 ml distilled water. 0.5 ml of this solution is sufficient to raise the pH of 125 ml of dilute unbuffered waters to 11.

APPARATUS

A. Pye-Unicam 104 gas chromatograph (or equivalent) set up as follows:

    1. One 4-foot by 1/8" phenyl isocyanate Porasil C (80-100 mesh) chromatographic column.

    2. Nitrogen carrier gas at 30 ml/min.

    3. Hydrogen detector gas at 15 ml/min.

    4. Air detector gas at 300 ml/min.

    5 Column temperature 50 C.

    6. Detector signal to 200 mV full-scale; recorder at 0.5 inches/min.

B. Compressed Gases

    1. Two cylinders of "methane-free" nitrogen with regulators.

    2. One cylinder of hydrogen with regulator.

    3. One cylinder of air with regulator.

    4. One cylinder of methane with regulator.

C. Water sample containers

    1. 125 ml glass stoppered reagent bottles - or

    2. 50 ml all glass "interchangeable" syringes.

D. 50 ml disposable polypropylene syringe with 18 G-1" needle.

E. 10 ml glass serum vials.

F. Serum stoppers for 10 ml vials. Stoppers from Johns Scientific (Toronto, Ontario) are recommended for their low permeability.

G. "000" rubber stopper.

H. 1 ml disposable glass syringe with 26G - 1/2" needle.

I. "Suba Seal" #33 available from Canadian Laboratory Supplies.

PROCEDURE

Calibration of gas chromatograph

1. A volumetric flask (500 or 1000 ml) is filled to over-flowing with distilled water and stoppered with a #33 Suba seal. Two 26G needles are inserted through the seal and the flask inverted. Nitrogen is then added to the flask through one of the needles to displace liquid down to the volumetric mark, leaving distilled water in the "dead volume" of the flask. The needles are removed and the flask placed upright. A known volume of methane is then injected, by syringe and 26G - 1/2" needle, through the seal. The flask is then shaken for 30 seconds with the small amount of water facilitating mixing while not absorbing a significant amount of methane. The following standards are prepared.

   Standard A.   10 ml CH_4/1000 ml N_2 = 446.4 μmoles/liter of gas mixture.

   Standard B.   1 ml CH_4/1000 ml N_2 = 44.64 μmoles/liter.

   Standard C.   10 ml Standard B/500 ml N_2 = 8.95 $\times$ 10^{-1} μmoles/liter.

   Standard D.   1 ml Standard B/500 ml N_2 = 8.95 $\times$ 10^{-2} μmoles/liter.

2. Inject 0.2 ml of methane standard directly into the gas chromatograph using a disposable 1 ml syringe and a 26G - 1/2" needle. Standards A-D are used to calibrate the instrument.

Sample analysis

1. Adjust sample temperature to 20 C.

2. For samples collected in reagent bottles; 25 ml of sample water is drawn into a 50 ml plastic syringe through an 18G needle. This transfer must be carried out as soon as the sample bottle is unstoppered. The 18G needle is replaced by a 26G needle and 25 ml of methane-free nitrogen drawn into the syringe by inserting the needle into the nitrogen stream flowing through a length of surgical rubber tubing. The syringe is then temporarily sealed by inserting the needle tip into a rubber stopper.

   If a 50 ml glass syringe is used to collect the 25 ml sample

in the field, then 25 ml of nitrogen is drawn directly into the sampling syringe.

3. The syringe is agitated vigorously for 30 seconds to partition methane into the gas phase. The gas phase now contains nitrogen plus methane from the water sample.

4. A 10 ml serum vial is filled with distilled water and sealed with a serum stopper. The sample syringe is unsealed (remove rubber stopper from 26G needle) and its needle inserted through the serum stopper. A second 26G needle is then inserted through the serum stopper. The gas phase in the syringe is then injected into the inverted serum vial so as to displace all of the water. The injection of the 25 ml gas phase flushes out the 10 ml serum vial. Remove both of the needles from the serum stopper.

5. 0.2 ml of the contents of the serum vial are removed and injected into the gas chromatograph using a 1 ml disposable glass syringe. Three replicate injections can be made before methane concentration in the vial is significantly altered.

CALCULATIONS

1. The scale factor for CH_4 can be calculated as follows:

$$\text{Scale Factor } CH_4 = \frac{\text{concentration } CH_4 \text{ (μmoles/liter of gas mixture)}}{\text{peak height of standard}}$$

where peak height is (chart units) x (attenuation)

This factor is usually constant throughout the standard range and is approximately 5×10^{-8} μmoles/peak height unit.

2. The proportion of dissolved methane transferred to the vapour phase during syringe stripping can be calculated as follows:

$$x = \frac{m}{1 + \dfrac{\alpha V_1}{V_g}}$$

where:

V_1 is the volume of the liquid phase
V_g is the volume of the gas phase
α is the solubility of methane at STP
    ($\alpha = 0.0332$ ml/ml H_2O @ 20 C)
m is the volume of CH_4 (at STP) present in V_1
x is the volume of CH_4 (at STP) present in V_g

From this equation it can be calculated that for any
concentration of methane, a 1:1 gas-water mixture will
strip 96.8% of CH_4 into the gas phase at 20 C. Therefore
a correction factor of +3.2% must be applied to the above
analytical method as it determines CH_4 only in the vapour
phase of the syringe.

3. Sample methane concentration is calculated as

$$CH_4 \text{ (μmoles/liter)} = \frac{\text{Sample peak height x Scale factor}}{0.968}$$

NOTES

1. This method also has been used routinely for analysis of
dissolved ethylene and acetylene (Flett and Hamilton, 1975),
and could be used for any dissolved gas detected by flame
ionization, providing the solubility of the gas in water is
known.

2. If samples for dissolved gas analysis are to be kept for
more than a few minutes in syringes then glass syringes must
be used. Plastic syringes have been found to be very
permeable to many gases. (e.g. N_2, O_2, CH_4, $CH{\equiv}CH$, $CH_2{=}CH_2$
but not CO_2.)

3. Methane-free nitrogen is used as a stripping gas since it is
compatible with the N_2 carrier gas of the gas chromatograph.
If air (containing O_2) or helium is used for stripping, small
negative or positive peaks respectively, interfere with the
CH_4 peak at low CH_4 concentrations.

ACKNOWLEDGMENT

This method was developed by J.W.M. Rudd and R.J. Flett of the
Freshwater Institute for which we thank them. It is published with
their permission.

SELECTED REFERENCES

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Rudd, J.W.M. and R.D. Hamilton. 1976 . Two samplers for monitoring dissolved gases in the lake water and sediments. Limnol. Oceanogr. 20:902-906.

AMMONIA-NITROGEN (MANUAL METHOD)

PRECISION

     Level   - 400 $\mu g NH_3$-N/liter

     Standard deviation - ±5 $\mu g NH_3$-N/liter

OPERATING RANGE   - 5-1000 $\mu g NH_3$-N/liter

SAMPLE CONDITION   - Unfiltered (See Note 1) stored at 5 C.
                        - Less than 24 hours old.
                        - Free from H_2S (If present, acidify sample to pH 3 and bubble with helium until free of sulphide odour).

METHOD PRINCIPLE   - Ammonia reacts with phenol and hypochlorite under alkaline condition to form indophenol blue; the colour intensity being proportional to ammonia concentration. Nitroprusside is used as a catalyst to facilitate colour development at room temperature. While the exact nature of the reaction is in some doubt, the order of reagent addition appears to be important. The order of reagent addition outlined below is that recommended by Solorzano (1969) and has been found to perform quite reliably.

REAGENTS

    A. Distilled and deionized water

        Pass distilled water over a strong acid cation exchange resin in hydrogen form. Prepare fresh as needed.

    B. Hypochlorite stock - Commercially available household bleach (5.5% available chlorine). This reagent deteriorates with time and should be checked periodically. Normality should be at least 1.5.

Note 1. Unfiltered sample is used to avoid undue exposure of samples low in NH_3 to lab atmosphere which often contains significant levels of NH_3.

C. Alkaline stock solution

Sodium citrate	100 g
Sodium hydroxide	5 g

Dissolve and make to 500 ml with distilled and deionized water.

D. Oxidizing reagent

Prepare fresh daily from 4 parts of C plus 1 part of B. Keep in stoppered bottle until used.

E. Sodium nitroprusside reagent

Dissolve 1.0 g sodium nitroprusside in distilled and deionized water, and make to 200 ml.

F. Phenol reagent

Dissolve 100 g phenol in 95% ethanol, and make to 1 liter.

G. Ammonium standard

Dissolve 3.818 g of dry ammonium chloride in distilled and deionized water and make to 1 liter.

$1.00 \text{ ml} = 1000 \text{ µg } NH_3\text{-N}$

APPARATUS

A. 50 ml stoppered graduated cylinders.

PROCEDURE

1. Prepare duplicate 100 ml aliquots of ammonia standard having a concentration approximating that of samples to be analyzed.

2. Place 50.0 ml of distilled and deionized water, ammonia standards or sample(s) in 50 ml stoppered graduates.

3. Add 2.0 ml of phenol reagent F. Mix.

4. Add 2.0 ml of nitroprusside reagent E. Mix.

5. Add 5.0 ml of oxidizing reagent D and mix by inverting the stoppered cylinders.

6. Between 1 and 24 hours later measure:

E_{B1} = Absorbance of distilled water plus reagents.

E_1 = Absorbance of standards and samples plus reagents.

Absorbance is measured at 640 nm using an appropriate path length for the level of ammonia present.

i.e. 1 cm path length 0-1000 μgNH_3-N/liter
       5 cm path length 0-200 μgNH_3-N/liter
      10 cm path length 0-20 μgNH_3-N/liter

CALCULATIONS

1. Unit extinction factor F for ammonia-N is calculated as follows:

$$F = \frac{\text{Concentration of std. } (\mu gNH_3\text{-N/liter})}{E_1 \text{ (standard) } - E_{B1}}$$

This should be around 1000 μgNH_3-N/liter for a 1.00 cm path length.

2. The concentration of ammonia-N in samples can be calculated by multiplying the extinction due to ammonia in the sample:

i.e. E_1 (sample) - E_{B1}

by the unit extinction factor F obtained above.

SELECTED REFERENCES

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Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 14:799-801.

AMMONIA NITROGEN (AUTOMATED METHOD)

PRECISION

      Level   - 600 $\mu g NH_3$-N/liter

      Standard deviation   - ± 12 $\mu g NH_3$-N/liter

OPERATING RANGE   - 10-1000 $\mu g NH_3$-N/liter

SAMPLE CONDITION
- Same as for manual method.
- Samples containing much suspended matter require filtering.

METHOD PRINCIPLE   - Same as for manual method.

REAGENTS

A. Distilled and deionized water. See manual method for details.

B. Buffer

Potassium hydrogen phosphate	200 g
EDTA (disodium dihydrate)	5 g
Sodium citrate	1 g
Sodium hydroxide (1 N)	130 ml

    Dissolve dry reagents in order given in 800 ml of distilled and deionized water. Add 1 N sodium hydroxide and make to 1 liter with distilled and deionized water.

C. Phenol stock

    Dissolve 625 g phenol in methanol and make to 1 liter.

D. Sodium hydroxide stock

    Dissolve 270 g of sodium hydroxide pellets in distilled and deionized water. When cool, make to 1 liter with distilled and deionized water.

E. Phenate reagent

>   Dilute 200 ml of phenol stock plus 450 ml of sodium
>   hydroxide stock to 1 liter with distilled and deionized
>   water.

F. Nitroprusside reagent

>   Dissolve 1.0 g sodium nitroprusside in distilled and
>   deionized water and make to 1 liter. Store in low
>   actinic glass bottle.

G. Hypochlorite

>   Dilute commercial bleach with 6 parts distilled and
>   deionized water to 1 part bleach. Prepare daily.

APPARATUS

1. Technicon Autoanalyzer[R] or comparable equipment (sampler,
   proportioning pump, colorimeter and recorder). Flow
   colorimeter should be equipped to measure absorbance at
   640 nm.

2. Using the manifold arrangement of Figure 16:

   A. Set the sampler rate to 20-40 samples per hour with a
      sample to wash ratio of 1:2.

   B. With the sample tube drawing distilled deionized water
      allow the system to equilibrate for 30 minutes.

   C. With the system sampling distilled deionized water,
      balance and zero the colorimeter. This automatically
      subtracts E_{B1} from all subsequent readings (See Note 1).

3. Place samples and standards on the sampler turntable and
   start sampler. Each group of 20 samples should be preceded
   and followed by pairs of standards.

4. Obtain absorbance values (E_1) for samples and standards.

Note 1. E_{B1} should be zero initially but may show positive drift as
reagents absorb NH_3 from room air.

AMMONIA MANIFOLD

SAMPLER
30 PER HOUR
1:2 SAMPLE TO
WASH RATIO

TO WASTE

TIME
DELAY
COIL

TO FLOW
CELL PUMP
TUBE

RECORDER

COLORIMETER
640 nm
15 mm F/c

SMC SMC SMC SMC

SAMPLE 0.80 ml/MIN

AIR 0.42 ml/MIN.

PHENATE 0.42 ml/MIN.

NH$_3$ BUFFER 0.32 ml/MIN.

HYPOCHLORITE 0.23 ml/MIN.

NITROPRUSSIDE 0.42 ml/MIN.

TO SAMPLER WASH RECEPTACLE DISTILLED DEIONIZED WATER 1.6 ml/MIN.

TO WASTE 2.00 ml/MIN FROM FLOW CELL

FIGURE 16.

75
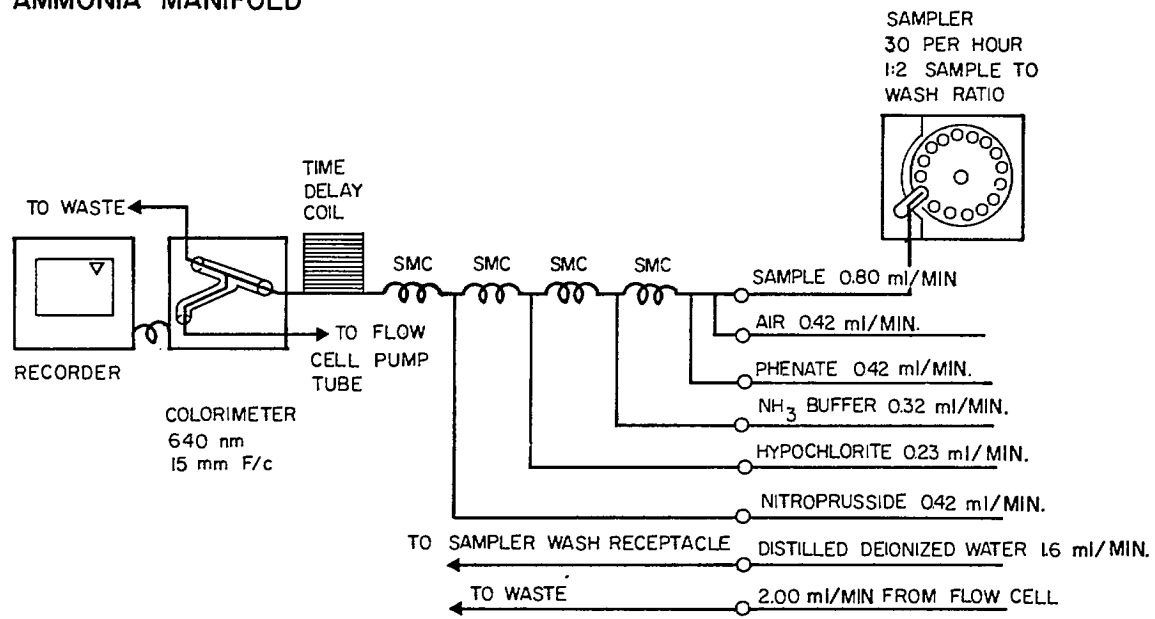
CALCULATIONS

1. The unit extinction factor for ammonia -N is calculated as follows:

$$F = \frac{\text{Standard concentration } (\mu gNH_3\text{-N/liter})}{E_1 \text{ (standard)} - E_{B1}}$$

This factor should be around 2000 μgNH_3-N/liter.

2. Concentrations of ammonia -N in samples can be calculated by multiplying the extinction due to NH_3 in the sample;

i.e. E_1 (sample) - E_{B1}

by the unit extinction factor F from above.

SELECTED REFERENCES

Harwood, J.E. and D.J. Huyser.   1970.   Automated analysis of ammonia in water. Water Res. 5:695-704.

See also manual ammonia method references.

NITRITE AND NITRATE NITROGEN (MANUAL METHOD)

PRECISION

Nitrate Level	-- $120 \ \mu gNO_3$-N/liter
Standard deviation	-- $\pm 4 \ \ \mu gNO_3$-N/liter
Nitrite Level	-- $5.0 \ \mu gNO_2$-N/liter
Standard deviation	-- $\pm 0.5 \ \mu gNO_2$-N/liter

OPERATING RANGE   -- 1-500 μgNO_3-N or NO_2-N per liter.

SAMPLE CONDITION
- Filtered through ignited Whatman GF/C.
- Stored at 5 C.
- Less than 48 hours old.
- Acid buffering capacity of sample must not exceed the alkaline buffering capacity of Reagent "A" below.

METHOD PRINCIPLE
- Acidification (0.02 N HCl) of a solution of nitrite yields nitrous acid. By addition of an aromatic amine (sulphanilamide) a diazonium salt forms which quantitatively couples with a second aromatic amine, N-1-naphthylethylenediamine-dihydrochloride   This coupling yields a pink azo dye with an absorbance maximum at 543 nm. Beer's law is obeyed.

  Nitrate in alkaline-buffered solution (pH-8) can be quantitatively reduced to nitrite by a cadmium-copper couple. The resulting nitrite can then be determined by forming the pink azo dye mentioned above.

REAGENTS

A. Buffer solution

> | Ammonium chloride | 100 g |
> |---|---|
> | Sodium tetraborate | 20 g |
> | EDTA (disodium dihydrate) | 1 g |

> Dissolve in distilled water and make to 1 liter.

B. Sulphanilamide

> Dissolve 5 g of sulphanilamide in a mixture of 100 ml of concentrated HCl and 300 ml of distilled water. Make to 500 ml with distilled water.

C. N-1-naphthylethylenediamine dihydrochloride (NNED)

> Dissolve 0.5 g of NNED in 500 ml of distilled water. Store in a low actinic glass bottle (dark brown or deep red). Renew if reagent develops a dark brown coloration.

D. Nitrate standard

> Dissolve 0.722 g of potassium nitrate in distilled water and make to 1 liter. Stable 2 months.
>
> 1.00 ml = 100 μg NO_3-N

E. Nitrite standard

> Dissolve 0.4926 g of sodium nitrite in distilled water. Make to 1 liter. Stable 2 months.
>
> 1.00 ml = 100 μg NO_3-N

F. Cupric sulphate

> Dissolve 20 g of cupric sulphate penta-hydrate in 1000 ml of distilled water.

G. 2 N Hydrochloric acid

> Dilute 85 ml of concentrated HCl to 500 ml with distilled water.

H   Cadmium filings - about 0.5 mm diameter.

APPARATUS

1. 50 ml stoppered graduated cylinders.

2. Cadmium-copper reduction column (See Figure 17) prepared as follows. Prepare filings for all columns in one batch. Quantities are for one column.

   A. Place 5 g of cadmium filings in a beaker, wash with 25 ml of 2 N HCl and rinse with distilled water.

   B. Add 10 ml of cupric sulphate solution and swirl until all copper is deposited (blue colour disappears).

   C. Plug bottom of column(s) with a small piece of glass wool, fill columns with water and add treated cadmium to a point level with the outlet. There should be no entrapped air bubbles.

   D. Flush column twice with a solution of 50 ml of distilled water plus 5 ml of buffer solution A.

   E. Adjust metering valve(s) so that the delivery rate for 25 ml is 240 seconds ±10 seconds.

PROCEDURE

NITRITE NITROGEN

1. Prepare, duplicate 100 ml aliquots of nitrite standard having a concentration approximating that of the samples to be analyzed.

2. Place a 50 ml of: distilled water, nitrite standards, or sample(s), into stoppered graduated cylinders. Add 5.0 ml of buffer solution (A) and mix by inverting the stoppered cylinders. (See Note 1).

3. Add 1.0 ml of sulphanilamide solution (B) and mix.

4. After 5 minutes add 1.0 ml of NNED solution (C) and mix.

5. Between 10 minutes and 2 hours later measure:

Note 1. Addition of buffer though unnecessary allows use of nitrate reagents and simplifies correction for NO_2 levels when computing NO_3.
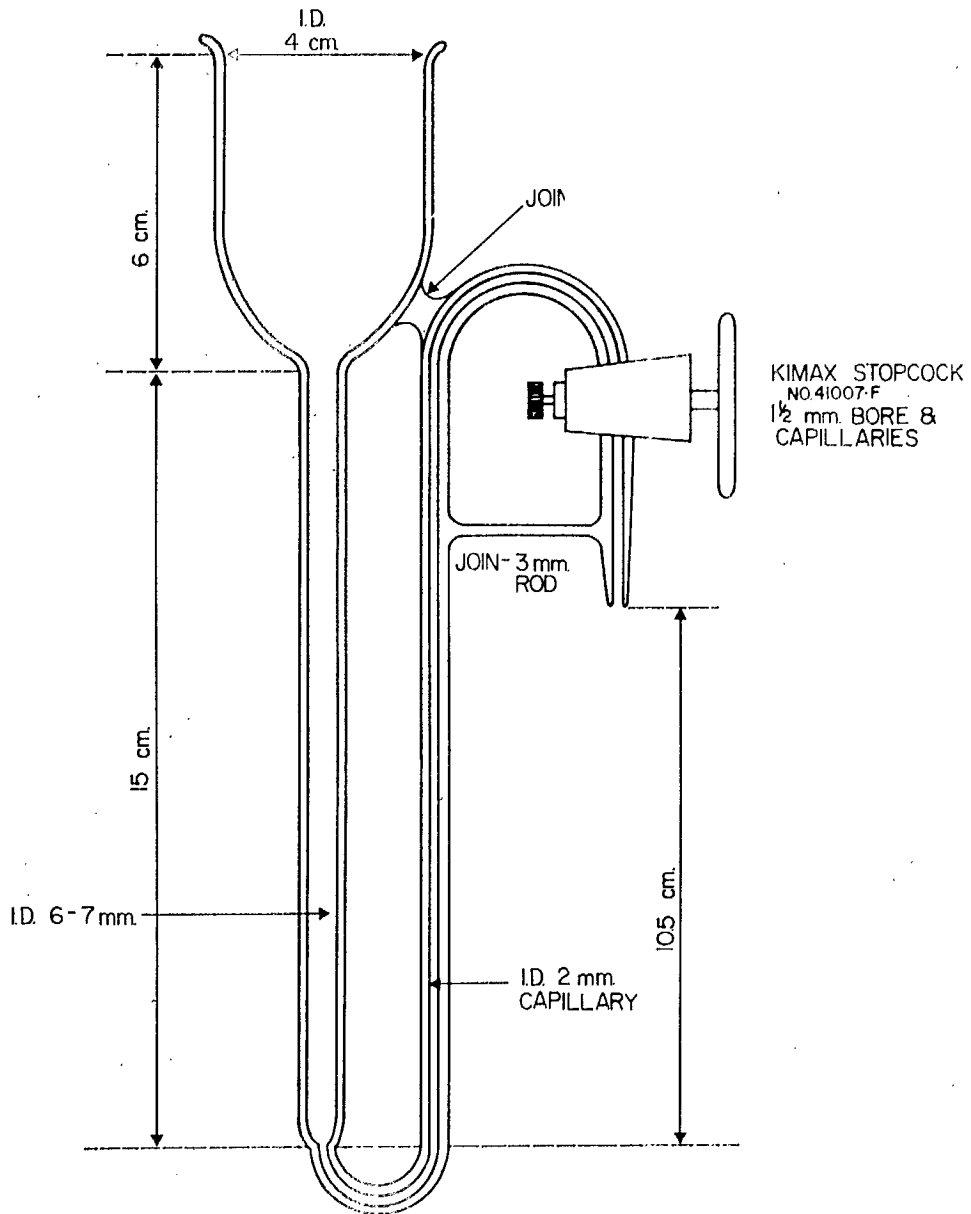
NITRATE REDUCTION COLUMN - BOROSILICATE GLASS

FIGURE 17.

E_{Bl} = Absorbance of distilled water + reagents

E_o = Absorbance of sample without NNED reagent (i.e. the natural color of the sample). (See Note 2).

E_1 = Absorbance of standards and samples with reagents.

Absorbance is measured at 543 nm using a path length appropriate for the level of nitrite present.

i.e.   1 cm path length   60-300 μgNO_2-N/liter
       5 cm path length   30-60 μgNO_2-N/liter
      10 cm path length   0-30 μgNO_2-N/liter

CALCULATIONS

1. Unit extinction factor F for nitrite -N is calculated as follows:

$$F = \frac{\text{Standard concentration } (\mu gNO_2\text{-N/liter})}{E_1(\text{standard}) - E_{Bl}}$$

This should be around 330 for a 1.00 cm path length.

2. The concentration of nitrite -N in samples can be calculated by multiplying the extinction due to nitrite -N in the sample;

i.e. E_1 sample - $(E_o + E_{Bl})$

by the unit extinction factor calculated above.

NITRATE NITROGEN

1. Prepare in duplicate enough nitrate standard to provide 50 ml for each cadmium-copper reduction column (Figure 17) to be used. Concentration should approximate that of the samples to be analyzed.

Note 2. E_o must be measured where water samples show visible brownish coloration.

2. Place 50 ml of distilled water, nitrate standard or sample(s) into stoppered graduated cylinders. Add 5 ml of buffer solution (A) and mix by inverting the stoppered cylinders.

3. Place 10 ml of buffered sample on the column, allow it to run through and discard the effluent.

4. Add remainder of buffered solution to the column, collect 2 ml of effluent in the same cylinder; rinse and discard. Collect 25 ml of column effluent.

5. Carry a distilled water blank and a standard through each column used.

6. Add 0.5 ml of sulphanilamide (B) to the 25 ml of column effluent and mix.

7. After 5 minutes add 0.5 ml of NNED (C) solution and mix.

8. Between 10 minutes and 2 hours later measure:

E_{B1} = Absorbance of distilled water plus reagent

E_o = Absorbance of sample without NNED reagent (natural color). (See Note 1.)

E_1 = Absorbance of standards and samples plus reagents.

Absorbance is measured at 543 nm using a path length appropriate for the level of nitrate present.

i.e. 1 cm path length   60-300 μgNO_3-N/liter
     5 cm path length   30-60 μgNO_3-N/liter
   10 cm path length   0-30 μgNO_3-N/liter

Note 1. E_o must be measured where water samples show visible brownish coloration.

CALCULATIONS

1. Unit extinction Factor for NO_3-N is calculated as follows:

$$F = \frac{\text{Standard concentration } (\mu g NO_3 \text{-} N / \text{liter})}{E_1 \text{ (standard)} - E_{B1}}$$

This should be around 330 for a 1.00 cm path length.

Unit extinction factors should be obtained for standards passed through each of the columns in use. Values should agree within 3%. If so, a mean is taken.

2. The concentration of nitrate -N in samples can be calculated by multiplying the extinction due to NO_3-N in the sample

i.e. E_1 samples - $(E_o + E_{B1})$

by the unit extinction factor calculated above.

3. Reduction efficiency of cadmium-copper column can be determined by measuring the extinction of a 100 μg/l NO_3 standard, and a 100 μg NO_2 standard. Efficiency should be above 95%. If not re-pack the column(s).

4. If NO_2-N is present in the sample it will be measured as NO_3 and results will be $NO_3 + NO_2$ nitrogen. If NO_2-N is present in significant amounts relative to NO_3-N it must be determined separately and nitrate values corrected as follows:

Given   1)   concentration NO_3-N + NO_2-N = x

        2)   concentration NO_2-N = y

        3)   reduction column efficiency % = Z

then $NO_3\text{-}N = x - [\frac{100}{z}]y$

If reduction columns are close to 100% efficient

            $NO_3\text{-}N = x - y$

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NITRITE AND NITRATE NITROGEN (AUTOMATED METHOD)

PRECISION

Nitrite Level	- 300 μgNO_2/liter
Standard deviation	- ± 1 μgNO_2/liter
Nitrate Level	- 300 μgNO_3-N/liter
Standard deviation	- ± 1 μgNO_3-N/liter

OPERATING RANGE   - 1-500 μg (NO_2-N or NO_3-N)/liter

SAMPLE CONDITION
- Same as for manual method.
- Sample must be free of sulphide which poisons the cadmium reduction column. See manual ammonia method "Sample Condition" for sulphide removal.

METHOD PRINCIPLE   - Same as manual method.

REAGENTS   - Same as manual method.

APPARATUS

1. Technicon Autoanalyzer[R] or comparable equipment (sampler, proportioning pump, colorimeter and recorder). Flow colorimeter should be equipped to measure absorbance at 540 nm.

2. Manifold assembled as in Figure 18.

3. In-line cadmium-copper reduction coil prepared as follows:

    A one meter length of 1 mm diameter cadmium wire (Koch-Light Laboratories Ltd. Colnbrook Bucks. England) is threaded inside a 1 meter length of 1/16" I.D. Teflon[R] tubing and wound into a 5 cm diameter coil. This coil is attached to two adjacent ports of a 4-way liquid chromatography valve (Pharmacia LV-4).

    The column is prepared for use by attaching the female luer coupling supplied with the valve to one of the remaining two

ports of the valve and injecting; from a syringe, through the cadmium column, 10 ml quantities of 1 N HCL, distilled water, 2% copper sulphate solution and distilled water, in that sequence at about 20 ml per minute. The valve and coil are then placed in line in the manifold of Figure 18. For details of column construction and performance see Stainton 1974 for details.

PROCEDURE

NITRITE

1. Prepare in duplicate 100 ml of nitrite standard having a concentration approximating that of the samples to be analyzed. Samples should be in the range 1-500 µg/liter NO_2-N. If concentration exceeds this, dilute with distilled water.

2. Using the manifold arrangement of Figure 18.

   A. Set the 3-way valve to bypass the cadmium-copper reduction column.

   B. Set sampler rate to 20-40 samples per hour with a sample to wash ratio of 1:2.

   C. With the sample tube drawing distilled water allow the system to equilibrate for 30 minutes.

   D. With the system sampling distilled water, balance and zero the colorimeter. This automatically subtracts the E_{B1} value from all subsequent readings. (See Note 1).

3. Add samples and standards to the sampler and start sampler. Each group of 20 samples should be preceeded and followed by pairs of standards.

4. Obtain absorbance values (E_1) for samples and standards.

5. If samples are visibly brownish their natural colour (E_0) must be measured. Replace the NNED reagent with distilled water. Allow the system to equilibrate for 10 minutes and reprocess samples to obtain E_0.

Note 1. E_{B1} should initially be set to zero but may drift during the course of a sample series in which case the drift must be included in calculations.

NITRATE - NITRITE MANIFOLD

SAMPLE
30 PER HOUR
1:2 SAMPLE TO
WASH RATIO

WASTE

RECORDER   COLORIMETER   LMC   SMC   BYPASS
            540nm.
            15 mm. F/C

TO FLOW
CELL
PUMP
TUBE

REDUCTOR

SAMPLE 0.80 ml /MIN.

BUFFER 0.16 ml/MIN.

AIR 0.42 ml/MIN.

SULFANILAMIDE 0.05 ml/MIN.

NNED 0.05 ml / MIN.

TO SAMPLE WASH RECEPTACLE   DISTILLED DEIONIZED WATER 1.6 mL/MIN.

TO WASTE   0.60 ml./MIN. FROM FLOW CELL

FIGURE 18.

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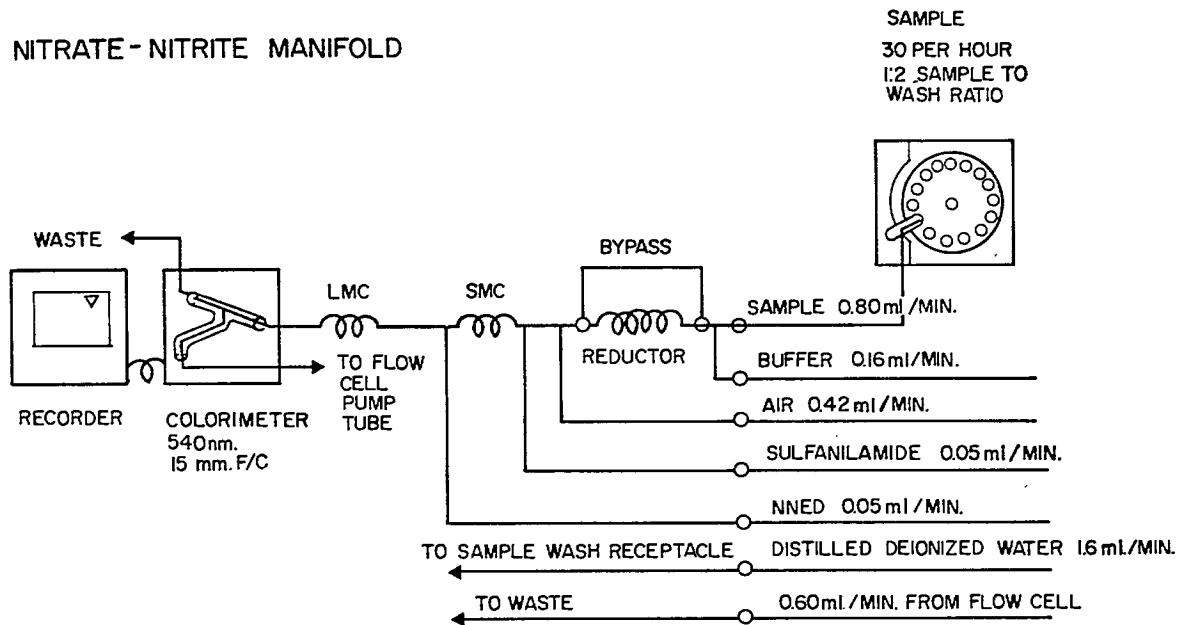
CALCULATIONS

1. The unit extinction factor for NO_2-N is calculated as follows:

$$F = \frac{\text{Standard concentration } (\mu g NO_2\text{-N/liter})}{E_1 \text{ (standard)} - E_{B1} \text{ (See Note 1)}}$$

This factor is around 500 $\mu g NO_2 ON$/liter for a 15 mm flow cell.

2. The concentration of nitrite -N in samples can be calculated by multiplying the extinction due to NO_2-N in the sample

i.e. E_1 (sample) $- (E_o + E_{B1})$

by the unit extinction factor F calculated above.

NITRATE

1. Prepare in duplicate 100 ml of nitrate standard having a concentration approximating that of the samples to be analyzed. Samples should be in the range 1-500 μg/liter NO_3. If sample concentration exceeds this, dilute with distilled water.

2. Using the manifold arrangement of Figure 18:

   A. Set the 3-way valve to incorporate the cadmium-copper reduction column into the flow system.

   B. Set sampler rate to 20-40 samples per hour with a sample to wash ratio of 1:2.

   C. With the sampling tube drawing distilled water, allow the system to equilibrate for 30 minutes.

   D. With the system sampling distilled water, balance and zero the colorimeter. This automatically subtracts the E_{B1} value from all subsequent readings. (See Note 1 automated nitrite method).

3. Add samples and standards to the sampler and start the sampler. Each group of 20 samples should be preceded and followed by pairs of standards.

4. Obtain absorbance values (E_1) for samples and standards.

5. If samples are visibly brownish their natural colour (E_o) must be determined. Replace NNED with distilled water. Allow the system to equilibrate for 10 minutes and reprocess samples to obtain E_o.

CALCULATIONS

1. The unit extinction factor for NO_3-N is calculated as follows:

$$F = \frac{\text{Standard concentration } (\mu g NO_3\text{-N/liter})}{E_1 \text{ (standard)} - E_{B1}}$$

The factor is around 500 $\mu g NO_3$-N/liter for a 15 mm path length.

2. The concentration of nitrate -N in samples can be calculated by multiplying the extinction due to NO_3-N in the sample

i.e. $\quad E_1 \text{ (sample)} - (E_o + E_{B1})$

by the unit extinction factor F calculated above.

3. Reduction efficiency of the cadmium-copper column can be determined by measuring the absorbance of a 100 $\mu g NO_3$-N/liter standard and a 100 $\mu g NO_2$-N/liter standard with the reduction column in line.

Efficiency may be anywhere from 60-100% depending upon age of column and sampling rate.

4. If NO_2-N is present in the sample it will be measured as NO_3-N and results will be NO_3-N + NO_2-N. If NO_2-N is present in significant amounts relative to nitrate it must be determined separately and nitrate values corrected as follows:

Given 1) concentration of NO_3-N + NO_2 = x $\mu g/l$

2) concentration of NO_2-N = y $\mu g/l$

3) reduction column efficiency = z%

then $NO_3-N = x - [\frac{100}{z}]y$

If reduction column is 100% efficient

$NO_3-N = x - y$

SELECTED REFERENCES

Brewer, P.G. and J.P. Riley. 1965. The automatic
determination of nitrate in sea water. Deep Sea Res.
12:765-72.

See also manual nitrate method references.

Stainton, M.P. 1974. Simple efficient reduction column
for use in the automated determination of nitrate in
water. Anal. Chem. 46:1616.

TOTAL DISSOLVED NITROGEN .

PRECISION

Level	- 640 µgN/liter
Standard deviation	- 13 µgN/liter

OPERATING RANGE — - 5-2000 µg/liter

SAMPLE CONDITION
- Filtered through Whatman GF/C.
- Stored at 5 C.
- Less than 48 hours old.
- Sample can be stored 5 days after photocombustion.

METHOD PRINCIPLE
- Under appropriate reaction conditions (pH 2 and adequate oxygen supply) organic nitrogen compounds can be decomposed by a 1-hour exposure to short UV radiation of high intensity. Products of the photocombustion are ammonia plus some nitrate and nitrite.

The photocombusted sample is passed through a zinc reduction column where nitrate and nitrite are reduced to ammonia. Total dissolved nitrogen is then measured as ammonia.

While the analytical procedure described is used to measure total dissolved nitrogen it can also be used to measure total inorganic nitrogen (i.e. the sum of NH_3, NO_2 and NO_3) by eliminating the UV decomposition step. Dissolved organic nitrogen can be estimated from the inorganic nitrogen difference between irradiated and non-irradiated samples. A manuscript (M.P. Stainton) providing greater detail of this method is in preparation.

REAGENTS - for photocombustion

A. Distilled and deionized water

Effluent from a "Barnstead Ultra Pure Mixed Bed" resin
column or a "Millipore Super Q" system typically contains
less than 30 µg/liter nitrogen.

B. Sulphuric acid 4 N - High purity

Prepare from high purity concentrated sulphuric acid.
"Ultrex" (J.T. Baker) and "Aristar" (B.D.H.) brands have
been found to have acceptable nitrogen levels.

C. Hydrogen peroxide

Reagent grade 30% w/w. This reagent deteriorates if left
open at room temperature. Store at 5 C. Caution: This is
a dangerous oxidant. Avoid contact with skin. Never orally
pipette. Wash hands after handling.

REAGENTS - for ammonia analysis

A. Distilled and deionized water   (See A above.)

B. Sulphuric acid 0.04 N

Dilute high purity concentrated sulphuric acid. (See B above.)

C. Zinc - 30-40 mesh

D. Complexing reagent

Potassium sodium tartrate	33 g
Sodium citrate	24 g
Distilled deionized water	1000 ml
Brij-35	0.5 ml

Dissolve tartrate and citrate in 950 ml of distilled water.
Adjust the pH of the solution to 5.0 with concentrated H_2SO_4.
Dilute to 1 liter with distilled and deionized water.
Add 0.5 ml of Brij-35.

E. Phenol stock

Dissolve 625 g phenol in methanol and make to 1 liter. Stable.

F. Sodium hydroxide stock

Dissolve 270 g of sodium hydroxide pellets in distilled and deionized water. When cool, make to 1 liter with distilled and deionized water. Stable.

G. Phenate reagent

Dilute 200 ml of phenol stock plus 450 ml of sodium hydroxide stock to 1 liter with distilled and deionized water.

H. Nitroprusside reagent

Dissolve 1.0 g sodium nitroprusside in distilled and deionized water and make to 1 liter. Store in low actinic glass bottle.

I. Hypochlorite

Dilute commercial bleach with 6 parts distilled and deionized water to 1 part bleach. Prepare daily.

APPARATUS - Photocombustion

A. Short UV irradiator

The apparatus used for this method consists of the following components:

1. 550 watt medium pressure mercury vapour lamp.

2. Cooling fan to prevent boiling of samples.

3. Quartz jacket tube to shield mercury lamp from the cooling effect of the fan.

4. Transformer to supply power at the correct voltage to the lamp.

5. Hour meter for lamp life monitoring.

6. On-off automatic timer.

←—QUARTZ LAMP JACKET

MERCURY VAPOUR—→ LAMP

QUARTZ SAMPLE TUBE

ALUMINUM HOUSING CUT AWAY TO SHOW INTERIOR DETAIL

FAN

HOUR METER

TIMER

ON OFF

CONTROL

TICKLER SWITCH

TRANSFORMER HOUSING

ON

FUSE

OFF
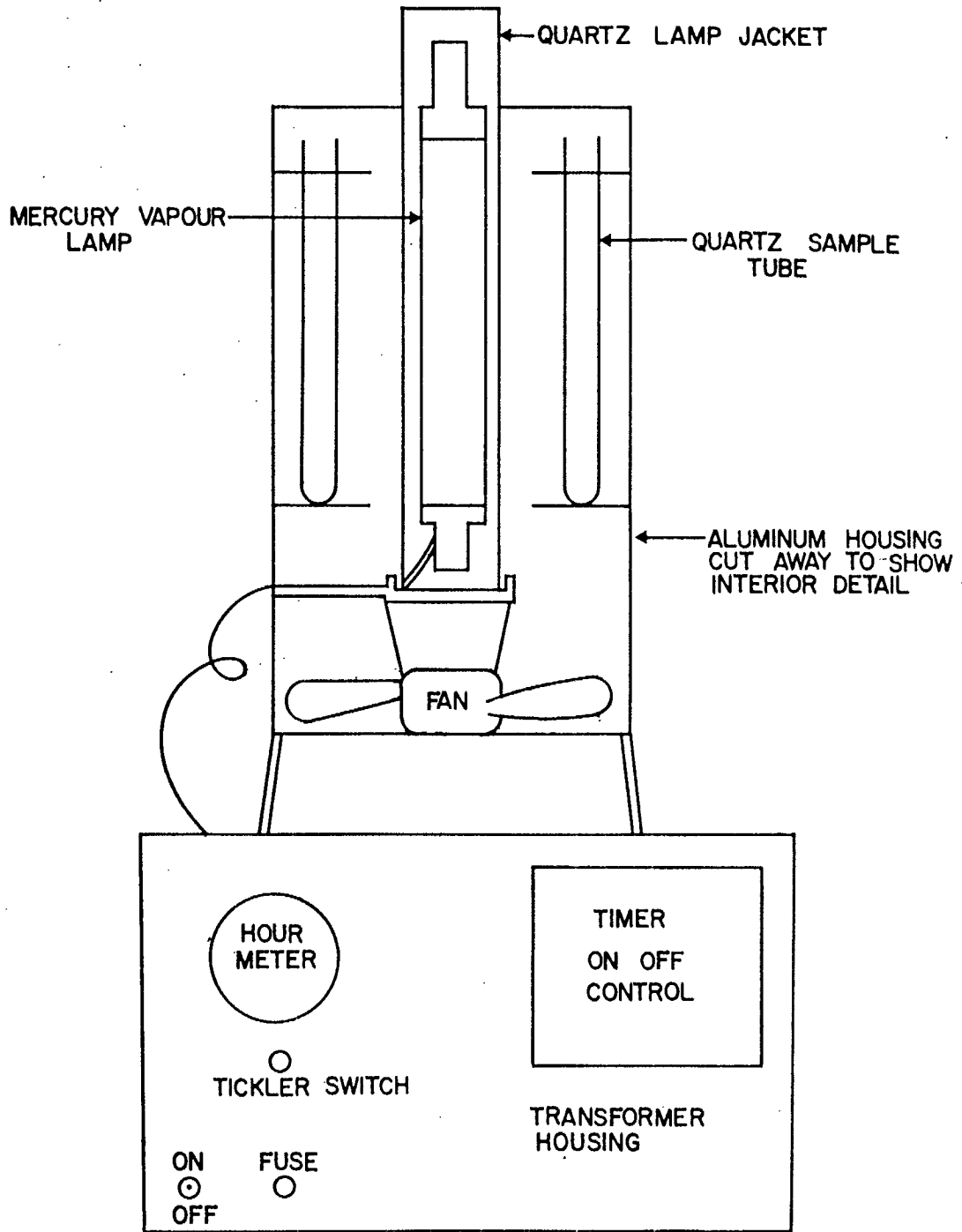
U.V. PHOTO OXIDIZER

FIGURE 19

7. Support assembly to hold lamp, fan, quartz jacket tube and samples in correct alignment and box to contain the transformer, timer and on-off control. See Figure 19.

Warm-up time is about 10 minutes for maximum energy output. If power is momentarily interrupted the lamp will not re-arc until cool.

PRECAUTIONS:

1. Do not look at arc with the naked eye or expose skin to arc for prolonged periods.

2. Do not handle quartz surface of lamp or quartz jacket tube with the fingers. Salt deposits ($NaHCO_3$ in particular) will permanently etch quartz surfaces, reduce their transparency, and hence the photocombustion efficiency.

3. Quartz surfaces should be wiped regularly with soft tissue, moistened first with distilled water, then ethanol.

B. Sample tubes

1. These are available in a wide variety of sizes. Size required depends on the quantity of sample available, the number of samples to be analyzed and the volume of liquid required for analysis. A convenient size is 30 ml which allows arranging 16 tubes in a 4.5 inch radius.

2. These quartz tubes should be treated with the same care outlined above for quartz surfaces.

3. No ink marking should be placed on the tubes. A diamond tip pen may be used to write identification on the tubes.

APPARATUS - for ammonia analysis

A. Technicon Autoanalyzer[R] or comparable equipment (sampler, proportioning pump, colorimeter and recorder). Flow colorimeter should be equipped to measure absorbance at 640 nm.

B. Manifold assembly as in Figure 20. Segmenting air for manifold should pass through an ammonia trap before entering pump tubing. See Figure 20.

C. Zinc reduction column.

Constructed from 5 mm I.D. glass tubing, 12 cm long. Pack column tightly with 30 mesh Zn and plug with glass wool. Additional zinc must be added to the column every 2-3 days of use.

PROCEDURE - photocombustion

1. Place 25 ml of filtered sample into a clean quartz tube.

2. Add 100 μl of 4 N H_2SO_4 (high purity).

3. Add 100 μl of peroxide.

4. Stopper tubes with glass marbles.

5. Place sample tubes in a previously "warmed up" irradiator and irradiate for 1 hour.

6. After completion of photocombustion allow samples to cool and make up to volume if evaporation has taken place.

7. Analyze samples for inorganic nitrogen. (See Note 1.)

8. If total N exceeds 2000 μg/liter, dilute sample with distilled and deionized water before photocombustion. Determine the blank of the dilution water also carried through the photocombustion stage.

Note 1. A portion of this irradiated sample can be used to determine total dissolved phosphorus. Please see total dissolved phosphorus method for details.

TOTAL DISSOLVED NITROGEN MANIFOLD
NITROGEN MEASURED AS AMMONIA

TO WASTE ◄

SAMPLER
30 PER HOUR
1:2 SAMPLE
WASH

Zn
REDUCTION
COLUMN

TO WASTE ◄

INCUBATOR
50 C

TO FLOW
CELL PUMP
TUBE

RECORDER   COLORIMETER
640 nm
15 mm F/C

SAMPLE .80 ml/MIN.

ACID .23 ml/MIN.

BUFFER .80 ml/MIN.

AIR .32 ml/MIN.

SAMPLE .60 ml/MIN.

PHENATE .42 ml/MIN.

HYPOCHLORITE .32 ml/MIN

NITROPRUSSIDE .42 ml/MIN

TO SAMPLER WASH RECEPTACLE   DISTILLED & DEIONIZED WATER 1.6 ml/MIN.

TO WASTE   FROM FLOW CELL 2.00 ml/MIN.

FIGURE 20

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PROCEDURE - inorganic nitrogen analysis   (See Note 2.)

1. Prepare duplicate 100 ml standards of ammonia and
   nitrate having a concentration of 1000 µg/liter N.

2. Using the manifold arrangement of Figure 20.

   A. Set the sampler at 20 per hour with a sample to
      wash ratio of 1:2.

   B. With the sample tube drawing distilled deionized
      water allow the system to equilibrate for 30 minutes.

   C. Balance and zero the colorimeter. This
      automatically subtracts E_{Bl}. (See Note 3.)

3. Add samples and standards to the sampler. A photocumbusted
   sample series should be preceded and followed by standards.

4. Peak heights for ammonia and nitrate standards should
   agree to within 5%. Reduction efficiency is usually
   98-100% but may deteriorate after several days of
   column use.

5. Obtain absorbance values to 3 decimal places (E_1) for
   samples and standards.

CALCULATION

1. The unit extinction factor for inorganic nitrogen
   $(NH_3 + NO_3 + NO_2)$ is calculated as follows:

   $$F = \frac{\text{Standard concentration } (\mu gN/liter)}{E_1 \text{ (standard)} - E_{Bl}}$$

Note 2. This is an automated method. For manual analysis of
         inorganic nitrogen, determine NO_3, NO_2, and NH_3 content
         of sample and sum the results.

Note 3. E_{Bl} should initially be set to zero but may drift during the
         course of a sample series and should be corrected for.

2. Concentration of inorganic nitrogen in samples can be calculated by multiplying the extinction due to $NH_3 + NO_3 + NO_2$ in sample.

    i.e. E_1 (sample) - E_{B1}

    by the unit extinction factor above.

3. Total dissolved nitrogen is equal to the inorganic nitrogen measured. An estimate of organic nitrogen can be obtained by measuring inorganic nitrogen before UV irradiation and subtracting this value from T.D.N. The difference is organic nitrogen.

4. If samples are diluted before irradiation then:

    $$C_1 = (C_2 \times D) - (C_3 \times (D-1))$$

    where

    C_1 = conc. of T.D.N. in sample
    C_2 = conc. of T.D.N. in diluted sample
    C_3 = conc. of T.D.N. in dilution water
    D = dilution factor.

SOLUBLE REACTIVE PHOSPHORUS

PRECISION

    Level   - 100 µg P/liter

    Standard deviation   - 1 µg P/liter

OPERATING RANGE   - 5-250 µg P/liter

SAMPLE CONDITION
- Filtered through Whatman GF/C. stored at 5 C.
- Unacidified.
- Less than 24 hours old.
- Less than 5 µg AsO_4^{-3}/liter.

METHOD PRINCIPLE
- Phosphate, silicate, arsenate and germanate ions react under acidic conditions with molybdate to form heteropoly acids which can be converted, by suitable reducing agents, to blue compounds of uncertain composition.

Using appropriate acid and molybdate strength, ascorbic acid as reductant and antimony as a color enhancing species, an intensely blue colored complex is formed with PO_4^{-3} and AsO_4^{-3} having an absorbance maximum at 885 nm.

It should be noted that, while the formation of the blue complex is specific to PO_4^{-3}, some observers feel that the reaction conditions are capable of hydrolysing labile organic phosphorus compounds. This would give an overestimate of PO_4-P and hence an unreliable estimate of biologically available phosphorus.

REAGENTS

A. Acid molybdate-antimony

Distilled water	500 ml
Ammonium paramolybdate $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$	7.5 g
Antimony potassium tartrate	0.14 g
Sulphuric acid (S.G. = 1.84)	88 ml

Mix in order given, cool and make to 1000 ml. Keep in dark glass bottle.

B. Ascorbic acid

Dissolve 2.5 g of L-ascorbic acid in 100 ml of distilled water. This reagent is stable for a few days if kept refrigerated.

C. Mixed molybdate for natural colour determination

Mix 4 parts of reagent A. with 1 part of distilled water.

D. Mixed molybdate for orthophosphate determination

Mix 4 parts of Reagent A. with 1 part of Reagent B. Stable 1 day.

E. Phosphate standard

Dissolve 0.2197 g potassium dihydrogen phosphate (KH_2PO_4) in 100 ml of water and make to 1000 ml with water saturated with chloroform.

$$1.00 \text{ ml} = 50.0 \text{ µg } PO_4\text{-P}$$

PROCEDURE

1. Prepare in duplicate 100 ml of orthophosphate standards having a concentration approximating that of the samples to be analyzed.

2. Place 25 ml of each standard or 25 ml of distilled water into 125 ml Erlenmeyer flask. Add 5.0 ml of mixed molybdate reagent D.

3. Place 25 ml of sample into a 125 ml Erlenmeyer flask. Add 5.0 ml of mixed molybdate reagent C.

4. Place 25 ml of sample into a second 125 ml Erlenmeyer flask. Add 5.0 ml of mixed molybdate reagent D.

5. After 5 minutes and within 3 hours measure

E_{B1} = Absorbance of distilled water + reagents.

E_o = Absorbance of sample without reductant.

E_1 = Absorbance of standards or sample with reductant.

Absorbance is measured at 885 nm using a 10.00 cm path length.

CALCULATIONS

1. Unit extinction factor for PO_4-P is calculated as follows:

$$F = \frac{\text{Standard concentration (µg P/liter)}}{E_1 \text{ (standard)} - E_{B1}}$$

This should be around 170 g PO_4-P/liter for a 10 cm path length. Concentration of soluble reactive phosphorus in sample can be calculated by multiplying the extinction due to reactive phosphorus in the sample

i.e. E_1 sample - $(E_o + E_{B1})$

by the unit extinction factor F calculated above.

SELECTED REFERENCE

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

SOLUBLE REACTIVE PHOSPHORUS (AUTOMATED METHOD)

PRECISION

Level	- 250 µg P/liter
Standard deviation	- ±1 µg P/liter

OPERATING RANGE — 1-500 µg P/liter

SAMPLE CONDITION — See manual method.

METHOD PRINCIPLE — See manual method.

REAGENTS

A. Ammonium molybdate

Dissolve 7.5 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) in 500 ml of distilled water. Add 0.14 g of antimony potassium tartrate ($KSbO \cdot C_4H_4O_6$), 88 ml conc. sulphuric acid, and 1 ml of phosphate standard (see Note 1). When cool dilute to 1 liter and store in dark glass bottle.

B. Ascorbic acid

Dissolve 2.5 g of L-ascorbic acid in 100 ml of distilled water. This reagent is stable for a few days if kept refrigerated.

C. Phosphate standard (See manual method)

1 ml = 50 µg PO_4-P

APPARATUS

Technicon Autoanalyzer [R] II system with manifold assembled as in Figure 21. System comprised of sampler, proportioning pump, manifold, colorimeter, recorder, and digital printer.

SOLUBLE REACTIVE PHOSPHORUS MANIFOLD

SAMPLER
40 PER HOUR
12 SECOND WASH

WASTE

37°C INCUBATOR

TO F/C PUMP TUBE

RECORDER

COLORIMETER
880 nm.
15 mm F/C

AIR 0.16 mL./MIN.

AMMONIUM MOLYBDATE 0.23 ml/MIN.

SAMPLE 1.20 ml/MIN

ASCORBIC ACID 0.10 ml/MIN.

DISTILLED WATER 2.00 ml/MIN.

TO SAMPLER

FROM FLOW CELL 0.80 ml/MIN.

TO WASTE
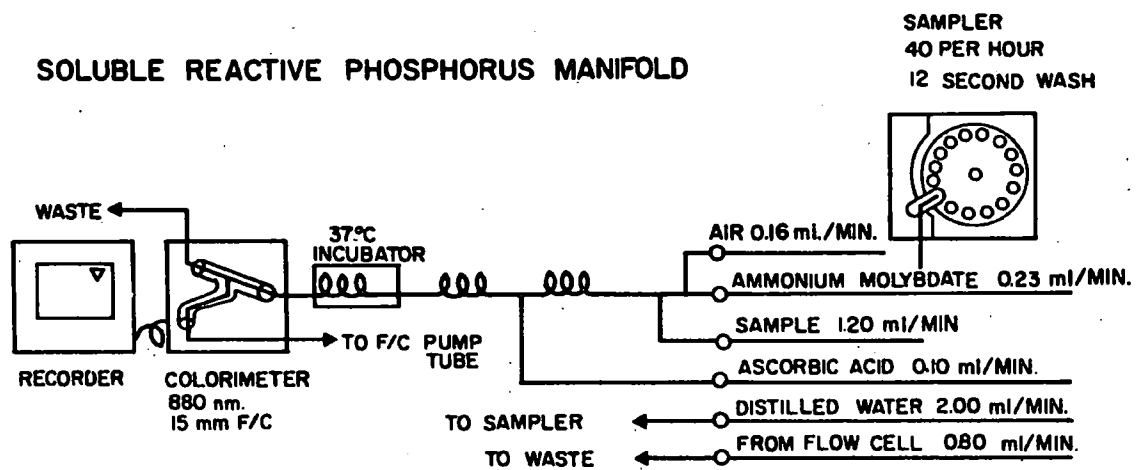
FIGURE 21.

PROCEDURE

Detailed instructions for the adjustment and calibration of the colorimeter and digital printer are given in the operating manual supplied with the equipment. The digital printer is adjusted to have a range of 0-500 and is calibrated with a 250 µg PO_4-P/l standard. Two or three samples of the standard should be allowed to pass through the system before calibration is attempted (See Note 1). The Sampling rate is set at 40 samples/hour with a wash time of 12 seconds.

Samples of concentration greater than 500 µg/l are diluted prior to analysis.

CALCULATIONS

For undiluted samples there are no calculations since the digital readout is in concentration. For diluted samples the digital readout value must be multiplied by the dilution factor.

NOTES

1. The molybdenum-blue complex may deposit on the flow cell causing the baseline to increase. This baseline drift gives erroneous results for the first 15-20 samples to pass through the system. The problem is almost completely eliminated by adding phosphate to the molybdate so that the concentration is approximately 50 µg PO_4-P/liter in the reagent. The molybdenum-blue complex is present in the system at all times and the baseline stabilizes after two or three samples have passed through the system.

2. This method is not recommended for the analysis of low levels of PO_4-P in natural waters that are coloured. The colour in the water usually absorbs quite strongly at the wavelength used for the PO_4-P analysis, giving high values for PO_4-P. For samples of this type the manual method is recommended as it involves a correction for natural colour.

SELECTED REFERENCES

See manual method for soluble reactive phosphorus.

TOTAL DISSOLVED PHOSPHORUS

PRECISION

      Level   - 20 μg P/liter

      Standard deviation   - 2.6 μg P/liter

OPERATING RANGE   - 5-250 μg P/liter

SAMPLE CONDITION
- Filtered through Whatman GF/C.
- Stored at 5 C.
- Less than 48 hours old.

METHOD PRINCIPLE
- Organic phosphorus compounds under acidic conditions, and with adequate oxygen supply, can be photo-oxidized to orthophosphate with short UV radiation. Breakdown is fairly quick (1 hour). This method does not, however, appear to hydrolyze polyphosphate. Resulting ortho-phosphate is measured by the soluble reactive phosphorus method. The photo-oxidation procedure is identical to that for total dissolved nitrogen. It is therefore possible to measure both TDN and TDP on a single photo-combusted sample.

REAGENTS

    See methods for total dissolved nitrogen and soluble reactive phosphorus.

APPARATUS

    See methods for total dissolved nitrogen and soluble reactive phosphorus.

PROCEDURE

The procedure for sample preparation and photo-combustion is the same as for total dissolved nitrogen. Photo-combusted samples are analyzed for soluble reactive phosphorus. Consult these two methods.

CALCULATIONS

The measured orthophosphate in photo-combusted samples is the total dissolved phosphorus content.

NOTE

If significant amounts of polyphosphates are suspected to be present the photo-combusted sample should be boiled with HCl prior to the orthophosphate analysis (Strickland & Parsons 1968).

SELECTED REFERENCES

Armstrong, F.A.J., and S. Tibbitts. 1968. Photochemical combustion of organic matter in sea water for nitrogen, phosphorus and carbon determination. J. Mar. Biol. Assoc.U.K. 48:143-152.

Henriksen, A. 1970. Determination of total nitrogen phosphorus and iron in freshwater by photo-oxidation with ultraviolet radiation. Analyst 95:601-605.

Stainton, M.P. The measurement of total dissolved nitrogen in fresh water using UV photodecomposition and detection of inorganic nitrogen. In Prep.

Strickland, J.D.H. and Parsons, T.R. (1968). A practical handbook of seawater analysis. Bull. Fish. Res. Board Can. 167:311 p.

PARTICULATE PHOSPHORUS

PRECISION

Level	- 25 µg P/liter
Standard deviation	- 1.5 µg P/liter

OPERATING RANGE
- 0.05-20 µg P per filter paper. Operating range in terms of water samples depends on the volume available or possible to filter.

SAMPLE CONDITION
- Water sample stored at 5 C with no acidification.
- Less than 48 hours old.
- Particulate collected on a preignited (16 hours at 550 C) Whatman 4.25 cm GF/C glass fiber filter paper.
- Damp filter placed in a glass screw cap vial. Vial stored at room temperature.

METHOD PRINCIPLE
- Particulate matter collected on a glass fiber filter is ignited at low temperature to destroy organic matter. The ignited filter is heated with dilute HCl which extracts the phosphorus and converts it to ortho-phosphate. Phosphorus is determined by a scaled down version of the soluble reactive phosphorus method.

REAGENTS

A.   1 N HCl

Dilute 83 ml of concentrated HCl to 1 liter with distilled water.

B.   Acid molybdate - antimony solution.

In 500 ml of distilled water dissolve in order listed:

Ammonium paramolybdate	7.5	g
Antimony potassium tartrate	0.14	g
Sulphuric acid	88	ml

Cool and make to 1000 ml. Store in a dark glass bottle.

C. Ascorbic acid

Dissolve 2.5 g of L-ascorbic acid in 100 ml of distilled water. This reagent is stable for a few days if kept in a refrigerator.

D. Mixed molybdate reagent

Mix 400 ml of reagent B with 100 ml of reagent C. Stable approximately 1 day.

E. Phosphate standard - stock

Dissolve 0.2197 g potassium dihydrogen phosphate in about 100 ml of distilled water and make to 1000 ml with water saturated with chloroform.

$$1.00 \text{ ml} = 50 \text{ µg } PO_4\text{-}P$$

APPARATUS

1. Spectrophotometer or colorimeter to read absorbance at 885 nm. A 1 cm flow-through cuvette is desirable.

2. Muffle furnace set at 550 C.

3. Oven set at 104 C.

4. Cornwall type dispensing syringes to deliver 10 ml and 2.5 ml.

5. Pyrex screw-cap vials, 20 ml capacity - 70 mm x 20 mm with screw caps and cap inserts.

6. Metal rack to hold the above vials and capable of standing 550 C.

7. Millipore type filtration apparatus to hold 47 mm filter papers.

8. Whatman GF/C glass fiber filter papers - 4.25 cm in diameter.

9. Microburette - 0.2 ml total volume to dispense phosphate standard.

PROCEDURE

1. Filter an appropriate volume (Vml) of sample through a 4.25 cm GF/C filter paper. Apply no more than 15 inches Hg vacuum and do not allow vacuum to remain on after samples have been sucked to dryness. Samples may be stored at room temperature for an indefinite period. It is convenient to store the filter paper in a pyrex screw-cap vial with identification on the lid. This pyrex storage container can then be used as the reaction vessel for the subsequent analysis for phosphorus.

2. Place sample vials, minus plastic lids, in a muffle furnace at 550 C for 1 hour to ignite organic matter. When processing samples include 4 blank papers in 4 separate vials to serve as blanks and standards.

3. After cooling, add 2 ml of 1 N HCl and 10 ml of distilled water to the ignited samples. Add 2.5 µg of PO_4-P to two of the blank papers included in step 2. Replace screw caps tightly and place in an oven at 104 C for 2 hours.

4. Remove samples from the oven and after cooling remove screw caps. Add 2.5 ml of mixed molybdate reagent to each vial. A rapid injection rate ensures mixing of reagent with sample.

5. Allow 30 minutes for color development (blue) and for glass fiber particles to settle.

6. Using a cuvette of appropriate path length (1-5 cm) measure absorbance of blanks, standards and samples at 885 nm.

CALCULATIONS

Having obtained

E_{Bl} = Absorbance of blank

E_1 = Absorbance of standard

E_o = Absorbance of sample

subtract E_{Bl} from standard and sample.

Using the standard absorbance corrected for blank, calculate a unit extinction factor in terms of µg of PO_4-P per sample vial:

$$i.e. \quad F = \frac{2.50 \ \mu g \ PO_4\text{-}P \ (per \ vial)}{E_1 - E_{Bl}}$$

Calculate µg PO_4-P per sample vial by multiplying the absorbance due to PO_4-P in samples by F

$$i.e. \quad PO_4\text{-}P/sample \ vial = F \ (E_o - E_{Bl})$$

To obtain the concentration of suspended P in the original water sample, multiply PO_4-P content of the vial by 1000/V where V is the volume, in milliliters, of water filtered through the glass fiber filter.

Note 1. The automated procedure for soluble reactive phosphorus outlined in this manual may be used to determine particulate phosphorus. Samples are processed up to the acid hydrolysis stage (Step 3 of above procedure) and analysed according to the automated technique.

SOLUBLE REACTIVE SILICON (MANUAL METHOD)

PRECISION

Level	- 400 µg Si/liter (diluted for analysis)
Standard deviation	- ±64 µg Si/liter

OPERATING RANGE

- 5-1500 µg Si/liter

SAMPLE CONDITION

- Unfiltered, stored in polyethylene at 5 C.
- DO NOT FREEZE. DO NOT STORE IN GLASS CONTAINERS.
- Less than 48 hours old.

METHOD PRINCIPLE

- Orthosilicate and possibly the dimer $(Si_2O_7^{-2})$ react with molybdate in acid solution to form heteropoly molybdates which can be reduced to silicomolybdenum blues. The absorption spectrum, intensity and stability of the color depend greatly on the acidity and other experimental conditions (Strickland 1951). In this method stannous chloride is used as reductant. Phosphate interference is prevented by the addition of tartrate which complexes excess molybdate, preventing its reduction. The absorption maximum is in the near infra-red (800-820 nm).

REAGENTS

A. Silica-free distilled water

A still pot with a silver plated or aluminum condenser will produce silica-free distilled water. Collect in polyethylene. Suitable water can also be produced by passing distilled water over a mixed bed ion exchange resin.

B.   Ammonium molybdate - 5% w/v

Dissolve 50 g of ammonium paramolybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in 1 liter of silica-free distilled water.

C.   Hydrochloric acid - approximately 1 N

Dilute 83 ml of concentrated HCl to 1 liter with silica-free distilled water.

D.   Mixed molybdate

Mix 2 volumes of molybdate reagent B. with 3 volumes of hydrochloric acid C. Prepare fresh daily.

E.   Tartaric acid - 10% w/v

Dissolve 100 g of tartaric acid in 1 liter of silica-free distilled water.

F.   Stannous chloride - stock - 3.5 N

Dissolve 40 g $SnCl_2\cdot2H_2O$ in 100 ml of 50% v/v HCl.

G.   Stannous chloride - 0.05 N

Prepare by dilution of stock stannous chloride. The normality of the final reducing solution should be between 0.04 and 0.06 and can be checked periodically by titration with standard iodine. Prepare fresh daily.

H.   Silicate standard

Grind a sample of quartz "Vitreosil", "Spectrosil", etc., to a fine powder. Heat powder to redness in a platinum crucible. Cool in a desiccator and weigh 0.107 g silica plus 0.6 g NA_2CO_3 into a platinum crucible. Heat to 800-1000 C in gas flame to melt flux and dissolve quartz completely (cessation of bubbles of CO_2 evolving from the transparent liquid flux). Cool and dissolve in silica-free distilled water. Make to 100 ml with silica-free water.

$$1.00 \text{ ml} = 500 \text{ μg Si}$$

APPARATUS

Spectrophotometer, or absorptiometer to measure extinction at 820 nm.

PROCEDURE

1. Prepare in duplicate 100 ml aliquots of silicate standard having a concentration approximating that of samples to be analyzed.

2. Place 3 ml of mixed molybdate reagent D in a 125 ml Erlenmeyer flask and add 50 ml of distilled water, silicate standard or sample and mix.

    Do not add sample to flask without first adding the acidic mixed molybdate. If the sample is alkaline a significant quantity of silicate can be solubilized from the flask.

3. Wait 15 minutes. (See Note).

4. Add 2 ml of tartaric acid E and mix.

5. Wait 2 minutes. (See Note).

6. Add 1 ml of stannous chloride reductant G and mix.

7. Between 5 minutes and 1 hour later measure:

    E_{B1} = Absorbance of distilled water plus reagents.

    E_1 = Absorbance of standards and samples plus reagents.

    Absorbance is measured at 820 nm using an appropriate path length:

1 cm path length	50-1500 µg Si/l
5 cm path length	25-250 µg Si/l
10 cm path length	5-100 µg Si/l

CALCULATIONS

1. Unit extinction factor for silicate is calculated as follows:

$$F = \frac{\text{Standard concentration } (\mu g \ Si/liter)}{E_1 \ (\text{standard}) - E_{B1}}$$

This should be around 1400 μg Si/liter for a 1 cm path length.

2. Concentration of soluble reactive silicon in samples can be calculated by multiplying the extinction of the sample.

i.e. $(E_1 \ Sample - E_{B1})$

by the unit extinction factor F calculated above.

NOTE

These times should be consistent for all samples and standards.

SELECTED REFERENCES

Armstrong, F.A.J. 1951. The determination of silicate in sea water. J. Mar. Biol. Assoc. U.K. 30:149-60.

Armstrong, F.A.J. and E.I. Butler. 1962. Chemical changes in sea water off Plymouth during 1960. J. Mar. Biol. Assoc. U.K. 42:253-58.

Strickland, J.D.H. 1952. The preparation and properties of silicomolybdic acid. (In three parts.) J. Am. Chem. Soc. 74:862-76.

SOLUBLE REACTIVE SILICON (AUTOMATED METHOD)

PRECISION

Level	-	2100 µg Si/liter
Standard deviation	-	±8 µg Si/liter
Level	-	10000 µg Si/liter (diluted for analysis)
Standard deviation	-	±44 µg Si/liter

OPERATING RANGE
- 5-1000 µg Si/liter for undiluted samples
- 1000-15000 µg Si/liter for diluted samples

SAMPLE CONDITION
- See manual method.

METHOD PRINCIPLE
- Same as manual method, except that ascorbic acid is used as a reductant.

REAGENTS

A. Silica-free distilled water

See manual method.

B. Ammonium molybdate

Dissolve 10 g of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in silica-free distilled water. Add 8.3 ml concentrated HCl and dilute to one liter. Store in amber bottle.

C. Tartaric acid

Dissolve 100 g of tartaric acid in silica-free distilled water and dilute to one liter.

D. Ascorbic acid

Dissolve 17.6 g ascorbic acid in silica-free distilled

water. Add 50 ml of acetone and dilute to one liter.
Add 0.5 ml of Levor IV.

E.   Silica standard

See manual method.

APPARATUS

Technicon Autoanalyzer^R II system with manifold assembled as in
Figure 22. System comprised of sampler, proportioning pump,
manifold, colorimeter, recorder, and digital printer.

Hook and Tucker Auto Diluter Mk II or equivalent.

PROCEDURE

Detailed instructions for the adjustment and calibration of the
colorimeter and digital printer are given in the operating
manual supplied with the equipment. The digital printer is
adjusted to have a range of 0-1000 and calibrated with a 500 µg
Si/liter standard. The sampling rate is set at 40 samples/hour
with a wash time of 12 seconds.

Samples of concentration greater than 1000 µg Si/liter are
diluted with a Hook and Tucker Auto-Diluter Mk II. The dilution
factor is obtained by diluting a 10,000 µg Si/liter standard and
running it in duplicate, with each batch of diluted samples.

CALCULATIONS

1.   For undiluted samples there are no calculations since the
      digital readout is in concentration.

2.   For diluted samples multiply the digital readout value by
      the dilution factor.

SELECTED REFERENCE

See manual method.

SOLUBLE REACTIVE SILICON MANIFOLD

SAMPLER
40 PER HOUR
12 SECOND WASH

TO WASTE

RECORDER   COLORIMETER
            660 nm
            50 mm F/C

SMC   SMC

TO FLOW CELL
PUMP TUBE

SAMPLE   0.32 ml/MIN.

AIR   0.23 ml/MIN.

MOLYBDATE   0.42 ml/MIN.

TARTARIC ACID   0.32 ml/MIN.

ASCORBIC ACID   0.42 ml/MIN.

TO SAMPLE WASH RECEPTACLE   DISTILLED DEIONIZED WATER 2.00 ml/MIN.

TO WASTE   1.00 ml/MIN. FROM FLOW CELL

FIGURE 22.

121
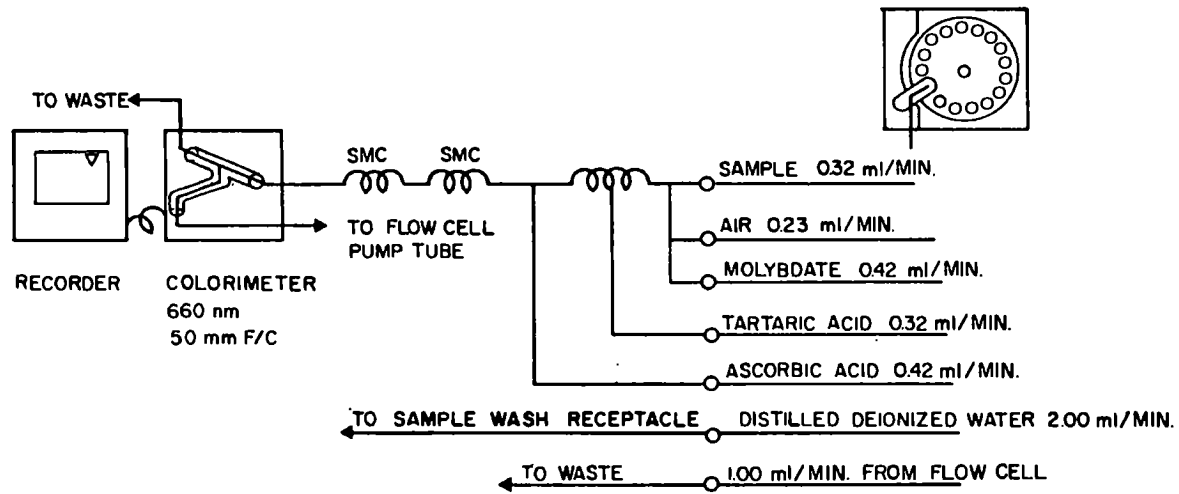
CHLORIDE (TITRIMETRIC)

PRECISION

Level - 30 mg Cl/liter

Standard deviation - ± 1 mg Cl/liter

OPERATING RANGE - 1.0 mg/liter upwards
1.00 ml of titrant ≡ 0.50 mg chloride

SAMPLE PREPARATION - Filtered through Whatman GF/C, stored at 5 C.
- Less than 30 days old.

METHOD PRINCIPLE - The sample is titrated with mercuric nitrate at pH 2.3-2.8, forming soluble, but undissociated, mercuric chloride with any chloride ion present. Excess mercuric ion reacts with diphenylcarbazone indicator forming a purple complex. Br^- and I^- respond in the same manner and hence interfere with this method. End point is pH dependent, therefore sample pH must be adjusted before analysis.

REAGENTS

A.   Chloride standard 0.0141 N

Dissolve 0.8241 g NaCl in distilled water and make to 1 liter.

1.00 ml = 0.50 mg chloride

B.   Nitric acid 0.1 N

Dilute 6.4 ml of HNO_3 to 1 liter with distilled water.

C.   Sodium hydroxide 0.1 N

Dissolve 4 g NaOH in distilled water and make to 1 liter.

D.   Indicator-acidifier reagent

s-Diphenylcarbazone   0.250 g
Concentrated nitric acid   4.0   ml
Xylene cyanol FF   0.030 g

Dissolve in order given in 95% ethanol. Make to 100
ml. Store in low actinic glass bottle at 5 C. Stable
several months.

E.   Standard mercuric nitrate titrant

Dissolve 2.3 g $Hg(NO_3)_2$ or 2.5 g $Hg(NO_3)_2 \cdot H_2O$ in
100 ml of distilled water containing 0.25 ml of
concentrated nitric acid. Dilute to 1 liter.

Solution is approximately 0.014 N in mercury. 1.00 ml
is approximately equivalent to 0.500 mg chloride.

APPARATUS

1.   Burette to contain 25 ml and graduated to nearest 0.1 ml.

2.   Magnetic stirrer with lighted base for ease of end-point
detection.

PROCEDURE

1.   Place 10.0 ml of standard sodium chloride solution in each
of three 125 ml Erlenmeyer flasks. Add 90 ml of distilled
water. These flasks contain 5.0 mg of chloride.

2.   Place 100 ml of distilled water blank in each of three
125 ml Erlenmeyer flasks.

3.   Place 100 ml of sample(s) in 125 ml Erlenmeyer flasks. If
samples are strongly alkaline or acidic adjust pH to
approximately 2.5 with 0.1 N nitric acid or 0.1 N sodium
hydroxide.

4.   Add 1.0 ml of indicator-acidifier reagent D to each standard,
blank, and sample. Color should be green-blue. If green,
the pH is too low. If blue, the pH is too high.

5. Titrate blanks, standards, and samples with mercuric nitrate to a definite purple colored end point. Record volume to the nearest 0.05 ml

V_{Bl} = Volume (ml) of titrant to blank end point

V_{Std} = Volume (ml) of titrant to standard end point

V_{sample} = Volume (ml) of titrant to sample end point

CALCULATIONS

1. An equivalence factor for the titrant can be calculated as follows:

$$F = \frac{5.0 \text{ mg Chloride}}{V_{Std} - V_{Bl}}$$

The factor should be around 0.50 mg chloride per ml of titrant.

2. Quantity of chloride in the sample flasks is calculated as follows:

Quantity of chloride = $(F)(V_{sample} - V_{Bl})$

3. Multiplication of the above value by 10 gives the concentration in mg chloride/liter in the original sample.

SELECTED REFERENCE

American Public Health Association. 1965. Standard methods for examination of water and waste water. 12th ed. APHA, New York, N.Y. 769 p.

CHLORIDE AND SULPHATE (AUTOMATED METHOD)

PRECISION

Chloride Level	-	10 mg Cl/liter
Standard deviation	-	±0.2 mg Cl/liter
Sulphate Level	-	10 mg SO_4/liter
Standard deviation	-	±0.2 mg SO_4/liter

OPERATING RANGE

- Chloride - 0.2-20 mg Cl/liter
- Sulphate - 0.2-30 mg SO_4/liter

SAMPLE PREPARATION

- Filtered through Whatman GF/C.
- Stored at 5 C.
- Less than 30 days old.

METHOD PRINCIPLE

Sample is divided into two portions, each being passed through an ion exchange column. (See Figure 23.) One half of the sample goes to column 1 (Figure 23) where a strong acid cation exchange resin exchanges sample cations for hydrogen ions. Effluent from column 1 is acidic and may contain HCl, H_2SO_4, HNO_3, H_3PO_4, H_4SiO_4, HF, and H_2CO_3. At low pH, only HCl, H_2SO_4, and HNO_3 are completely dissociated. Usually only HCl and H_2SO_4 are present at significant levels. Hydrogen ion concentration in the effluent from column 1 is therefore equivalent to chloride plus sulphate.

The other half of the sample goes to column 2 which contains a 2-stage resin bed. The first stage contains silver saturated resin. Silver exchanges for sample cations and precipitates chlorides as silver chloride. The second stage contains hydrogen saturated resin which exchanges silver for hydrogen ion. The resulting effluent is identical to that of column 1 except that HCl has been quantitatively removed. Hydrogen ion concentration in the effluent from 2 is equivalent to sulphate.

The difference in hydrogen ion concentration in the effluents of

columns 1 and 2 is equivalent to chloride.

Hydrogen ion concentration in column effluent is measured using a conductivity meter and a flow-through conductance cell with signal output to a strip chart recorder.

Since chloride and sulphate solutions of equivalent strength give equivalent response, only a sulphate standard is required to calibrate the response of both channels 1 and 2.

In some waters nitrate, orthophosphate and fluoride may be present at significant levels and their sulphate interference must be corrected for. See Table III for correction factors.

REAGENTS

A.   0.1 N HCl and 0.1 N $AgNO_3$ (Approximate concentrations only)

B.   Strong acid cation exchange resin

"Rexyn 101" or equivalent having a wet volume exchange capacity of 2.0×10^{-3} equivalents per ml. Mesh size 16-50.

C.   Sulphate standard

Dissolve 7.102 g of reagent grade Na_2SO_4 in distilled water and make to 1 liter.

1.00 ml = 100 μ equivalent sulphate
or chloride

APPARATUS

1.   Sampler, proportioning pump, 2 flow-through conductivity cells (cell constant 0.316/cm), 2 conductivity meters (500 μ Siemens full-scale), and a 2-channel strip chart recorder assembled as in Figure 23.

2.   Ion exchange columns constructed as in Figure 24 and prepared as follows:

A.   Columns packed with strong acid resin are saturated with hydrogen ion by pumping 0.1 N HCl through the column at 2 ml per minute for 20 minutes. Columns

CHLORIDE   SULPHATE   MANIFOLD
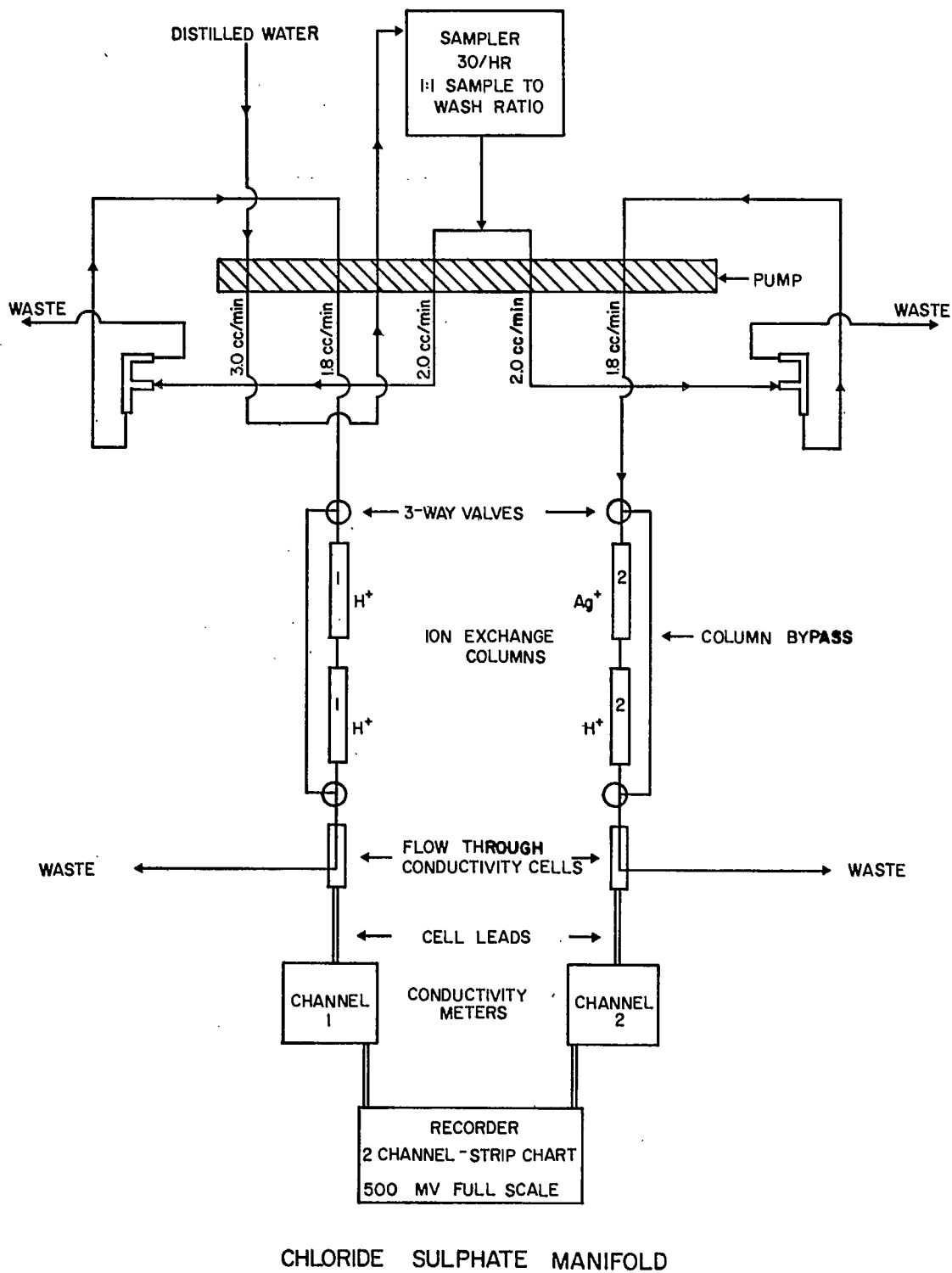
FIGURE 23.

ION EXCHANGE COLUMN

Male Luer Coupling

Tygon Tubing Sleeve

Glass Wool Plug

Strong Acid Cation
Exchange Resin
16-50 Mesh
Either Hydrogen or Silver
Saturated Depending on Use.

100 mm

Female Luer Coupling

8mm
O.D.
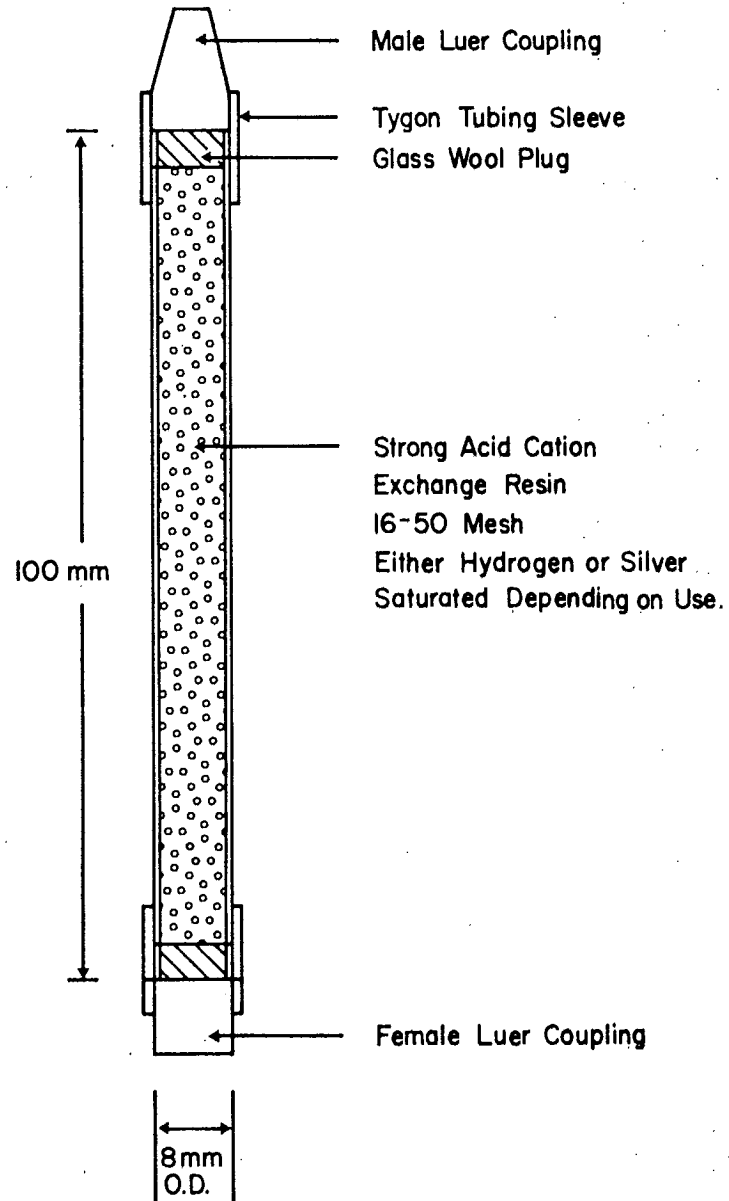
FIGURE 24.

are then rinsed with distilled water pumped at 2 ml per minute for 20 minutes. Three such columns are required for the manifold of Figure 23.

B. Silver columns were prepared as above using 0.1 N AgNO$_3$.

C. Life of columns depends on sample size, exchange capacity of resin used and ionic strength of samples analyzed, but should be at least 2000 samples.

D. Column 1 can be regenerated simply by treatment with 0.1 N HCl. The first stage of column 2 cannot be easily regenerated and is discarded. The second stage of column 2 contains much silver and should be used to prepare a silver saturated column.

PROCEDURE

1. Prepare duplicate sulphate standards containing 500 µeq sulphate/liter.

2. Set sampler at 30 per hour with a 1:1 sample to wash ratio.

3. While pumping distilled water through the system, zero recorders.

4. Place samples and standards on sampler and start sampler.

5. Obtain peak heights for standards and samples for channels 1 and 2.

CALCULATIONS

1. Compute a scale factor for channels 1 and 2.

    i.e. $F = \dfrac{\text{Standard concentration (µeq/liter)}}{\text{Peak height (chart units)}}$

    Factor should be approximately 7 for the system described.

2. Multiply sample peak height for channels 1 and 2 by their respective scale factor to obtain µeq/liter values for channels 1 and 2. Values for channel 1 are µeq chloride plus sulphate/liter. Values for channel 2 are µeq sulphate/liter. The difference between channels 1 and 2 is µeq

chloride/liter.

3. Chloride levels in µeq/liter are multiplied by 0.0355 to give mg chloride/liter.

4. Sulphate levels in µeq/liter are multiplied by 0.048 to give mg sulphate/liter.

The principle of this method can be used for the manual determination of chloride and sulphate. See Mackereth (1955a and 1955b).

ANION	SULPHATE INTERFERENCE
1 mg/liter	mg/liter
NO_3-N	3.42
F	2.53
PO_4-P	1.29
HCO_3-C	0.06
SiO_4-Si	no interference

Table III. Sulphate interference caused by various anions.

SELECTED REFERENCES

Mackereth, F.J.H. 1955a. Ion exchange procedures for the estimation of (I) total ionic concentration; (II) chlorides; and (III) sulphate in natural waters. Mitt. int. Ver. Limnol. 4:1-16.

Mackereth, F.J.H. 1955b. Rapid microestimation of the major ions of freshwater. Proc. Soc. Water Treat. Exam. 4:27-42.

Mackereth, F.J.H. 1963. Some methods of water analysis for limnologists. Freshwater Biol. Assoc. Sci. Publ. 21:70 p.

Stainton, M.P. 1974. An automated method for determination of chloride and sulphate in freshwater using cation exchange and measurement of electrical conductance. Limnol. Oceanogr. 19:707-711.

SULPHATE (GRAVIMETRIC METHOD)

PRECISION

     Level   – 50 mg SO_4/liter

     Standard deviation   – ±2 mg SO_4/liter

OPERATING RANGE   – 1-200 mg SO_4/liter

SAMPLE CONDITION
- Filtered through Whatman GF/C.
- Stored at 5 C.
- Less than 30 days old.

METHOD PRINCIPLE
- Hot barium chloride solution is added to boiling sample to precipitate barium sulphate. The precipitate is digested, collected on a filter paper, washed with boiling water and ignited. The resulting barium sulphate is weighed and sulphate concentration in the original sample calculated.

REAGENTS

A. Methyl red indicator

    Dissolve 100 mg methyl red (sodium salt) in 100 ml of distilled water.

B. Hydrochloric acid - 6 N

    Dilute concentrated HCl 1:1 with distilled water.

C. Barium chloride

    Dissolve 100 g of $BaCl_2 \cdot 2\ H_2O$ in 1 liter of distilled water. Filter before use.

       1 ml precipitates approximately 40 mg sulphate

APPARATUS

1. Muffle furnace set at 800 C.

2. Hot plate with control to maintain beakers of water at 80-90 C.

3. Porcelain crucibles to contain 10 ml.

4. Ashless filter papers. Whatman No. 42 - 11 cm diameter.

5. Filter funnels and rack.

PROCEDURE

1. Measure 100 ml of filtered sample into a 250 ml beaker and heat to boiling.

2. Add one drop of indicator.
   Add acid (B) until indicator turns red.
   Add 2 ml of acid (B) in excess.

3. Add slowly 5 ml of hot barium chloride solution.

4. Cover beaker with a watch glass and allow to digest at 80-90 C overnight.

5. Quantitatively transfer the barium sulphate precipitate to an ashless filter paper and wash the precipitate with hot distilled water.

6. Transfer the filter paper with precipitate to a pre-ignited (1 hour at 800 C), pre-weighed (nearest 0.1 mg) crucible.

7. Ignite crucible, paper and precipitate for 1 hour at 800 C.

8. Re-weigh the cool ignited crucible to the nearest 0.1 mg.

CALCULATIONS

1. Multiply the weight of barium sulphate precipitate (in mg) by 0.4115 to obtain the weight (mg) of sulphate in the 100 ml of sample used. Multiply this by 10 to obtain the sulphate concentration in mg sulphate/liter.

SELECTED REFERENCE

American Public Health Association 1965. Standard
methods for examination of water and waste water,
12th ed. APHA, New York, N.Y. 769 p.

SULPHIDE

PRECISION

    Level   - 330 µg Sulphide-S/liter

    Standard deviation   - ±11 µg Sulphide-S/liter

OPERATING RANGE   - 16-13,000 µg Sulphide-S/liter

SAMPLE CONDITION
- Unfiltered.
- 25 ml collected in a 30 ml glass syringe with a stainless steel 3-way valve.
- A second 25 ml sample is collected in a plastic liquid scintillation vial for measurement of natural color. (See section on sample collection.)
- Protected from light until analysis.
- Analyzed within 2-3 hours of collection.

METHOD PRINCIPLE
- Under acidic conditions sulphide sulphur, as H_2S, reacts with p-phenylenediamine dihydrochloride and ferric chloride to form a purple dye (Lauth's violet) having an absorbance maximum at 600 nm. Reagents are injected directly into the sample while contained in a syringe to avoid sulphide loss via oxidation or H_2S degassing. Lauth's violet is stable for several days although absorption will increase slowly with time.

REAGENTS (Standardization of sulphide stock)

    A.   Deoxygenated water

           Fill a one-liter flask almost to the mark with distilled water and deoxygenate by bubbling for one hour with oxygen-free nitrogen (see Ref. 1).

B.   Sodium sulphide - Make up just prior to standardization

> Sparingly wash with distilled water some crystalline sodium sulphide ($Na_2S \cdot 9H_2O$) and dry with a filter paper. Weigh out approximately 25 g and add to the deoxygenated water prepared above. Stir in the dark until dissolved. Store under refrigeration in a dark glass bottle. This solution deteriorates quite rapidly and must be standardized each time before preparing dilute standards. Store 1 week only.

C.   Starch indicator - See dissolved oxygen method.

D.   Sodium thiosulphate 0.025 N - See dissolved oxygen method.

E.   Iodine 0.025 N

> Dissolve 20-25 g of KI in 100 ml of distilled water and add 3.175 g iodine. Make to 1 liter.

REAGENTS (Sulphide analysis)

A.   p-phenylenediamine dihydrochloride

> Dissolve 1.2 g p-phenylenediamine dihydrochloride in 350 ml of distilled water. Add 100 ml of concentrated HCl. When cool make to 500 ml. Stable two weeks or longer if stored in dark and kept cool.

B.   Ferric chloride

> Dissolve 33.3 g of $FeCl_3 \cdot 6H_2O$ in 200 ml of concentrated HCl and make to 1 liter with distilled water. Store in stoppered glass bottle.

C.   Mixed reagent

> Immediately before analysis mix 5 parts of reagent A with 1 part reagent B.

D.   Hydrochloric acid 2.4 N

> Dilute 100 ml of concentrated HCl to 500 ml with distilled water.

E,   Sodium hydroxide 0.1 N

Dissolve 4 g of NaOH in distilled water and make to 1 liter with distilled water.

F.   Alkaline water for dilute sulphide standards

Add 1 ml of 0.1 N NaOH to 900 ml of deoxygenated distilled water and make to 1 liter. Use to prepare dilute sulphide standards. Alkaline pH prevents loss of sulphide as H_2S.

APPARATUS (Standardization of sulphide stock)

1.   Burette - 25 ml - with 0.1 ml graduations. .

2.   Magnetic stirring plate with light source in base.

APPARATUS (Sulphide analysis)

1.   30 ml syringes with glass barrels and tight fitting plastic plungers. One required for each blank, standard and sample.

2.   Stainless steel 3-way valves equipped with 2 female and 1 male Luer couplings. One required for each of above syringes.

3.   10 ml syringe - same design as 30 ml syringe. One required for dispensing mixed reagent.

4.   Spectrophotometer or absorptiometer to measure absorbance at 600 nm.

PROCEDURE (Standardization of sulphide stock)

1.   Add 10.0 ml of approximately 0.025 N iodine solution to a 125 ml Erlenmeyer flask and titrate with 0.025 N thiosulphate using a starch indicator. Repeat 6 times.

2.   Add 10.0 ml of sulphide stock to 125 ml Erlenmeyer flask and titrate with the iodine solution standardized above. Repeat 6 times.

3. Calculate normality of iodine solution using

   ml iodine x N iodine = ml thiosulphate x N thiosulphate

4. Similarly calculate the normality of the stock sulphide and convert to gram/liter units by multiplying sulphide normality by 16. The stock solution should contain about 3.2 g sulphide - S/liter.

PROCEDURE (Sulphide analysis)

1. Using the calibrated stock sulphide and previously prepared alkaline water, prepare 100 ml aliquots of dilute sulphide standard to cover the range of sample concentrations.

2. Draw 25 ml of distilled water (prepare two) or sulphide standards into 30 ml glass syringes. Samples are collected in 30 ml glass syringe and sealed with a 3-way valve. Avoid entrapment of air bubbles, protect from light and process immediately. It is essential to minimize contact with air and light as dilute sulphide solutions are quite unstable.

3. Inject 3 ml of mixed reagent through the valve into the syringes containing blanks, standards and samples using a 10 ml syringe as a reagent reservoir-dispenser. Shake syringes once immediately after addition of reagent and again a few minutes later. Process one of the distilled water blanks at the start and one at the end of the run.

4. Using the duplicate sample(s) collected for natural color measurement, add 3 ml of 2.4 N HCl to 25 ml of lake water (an Erlenmeyer flask is a suitable container).

5. Allow at least 10 minutes for color development before removing 3-way valves from syringes. Development may take longer for very cold samples. It is advisable to measure absorption as soon as possible after color development, particularly with samples having low concentrations. Samples having an absorbance greater than 1 can be diluted after color development.

6. Measure absorbance at 600 nm using a 1.0-5.0 cm path length:

   E_{Bl} = Absorbance of distilled water plus reagents

   E_o = Absorbance of sample plus acid only (natural color)

E_1 = Absorbance of sample + reagents

7. Unit extinction factor for sulphide-S is calculated as follows:

$$F = \frac{\text{Standard concentration (µg S/liter)}}{E_1(\text{Standard}) - E_{B1}}$$

Sulphide in sample is calculated by multiplying the extinction due to sulphide-S in sample

i.e. E_1 sample - (E_0 + E_{B1})

by the unit extinction factor F calculated above.

SELECTED REFERENCES

Macy, J.M., Sneller, J.E., and Hungate, R.E. (1972).
Use of syringe methods for anaerobiosis. American
Journal of Clinical Nutrition. 25:1318-1323.

Strickland, J.D.H. and Parsons, T.R. (1968). A
practical handbook of seawater analysis. Bull. Fish.
Res. Bd. Canada. No. 167. 311 pp.

ACKNOWLEDGMENT

METALS BY ATOMIC ABSORPTION AND EMISSION SPECTROSCOPY

OPERATING RANGE   - See individual metals.

SAMPLE CONDITION   - Stored at 5 C for less than 48 hours
                                     before filtering.
                                   - Filtered through Whatman GF/C.
                                   - Acidified with 1 ml 3 N HCl per 100
                                     ml of sample.
                                   - Do not freeze samples.

METHOD PRINCIPLE

An aqueous solution containing the metal of interest is aspirated
into a laminar flow, air-acetylene flame. At high temperature,
un-ionized metal atoms are either excited, emitting line spectra,
or are capable of absorbing radiant energy. Whether metals emit
or absorb radiation depends upon their ionization potential,
flame temperature and sample matrix.

For elements that are readily excited the flame is used as a
point emission source with emitted light being chopped and
passed through a slit and monochromator to a phototube. Emitted
light is proportional to concentration of emitting element.

For elements that absorb radiant energy the flame is analogous
to the cuvette of conventional UV-visible spectroscopy and is
placed between a light source and the slit, monochromator and
phototube assembly.

Sensitivity and specificity is obtained by using a source lamp
whose cathode contains the element of interest. Source lamp
emission is a line spectrum of which a principal line is
coincident with the principal absorption line of the element of
interest. Radiant energy absorbed is proportional to element
concentration, there usually being a linear relationship.

Significant interferences are of three types: ionization,
chemical and non-specific absorption.

Ionization interference occurs when the degree to which the
element of interest is ionized depends on other ionized metals
in the sample. The resulting signal, whether it be emission or

absorbance, is then dependent both on the level of the element of interest and the level of other ionizable metals present. Potassium, for example, when present in large excess to sodium, causes a decrease in the ionization of sodium which increases the emission signal and the absorbance signal. This form of interference can be overcome by matching the level of interfering metal in standards and samples.

Chemical interference occurs when the element of interest combines with other elements in the sample or flame. The signal is either enhanced or depressed depending on whether the compound formed is more labile or more refractory than the uncombined element. The net effect is an increase or decrease in the ground state atoms available for absorption. Methods for eliminating this interference depend largely on the element of interest and the interfering species. In the case of calcium and magnesium, phosphate interference is eliminated by adding excess lanthanum which preferentially forms a refractory compound with phosphate. Often a hotter flame temperature (nitrous oxide-acetylene) will dissociate refractory compounds.

Non-specific absorption occurs when the flame contains particles (salts and unevaporated solvent) which scatter light or molecules capable of absorbing over a broad spectral range. A false positive absorption error results. This can be corrected by measuring absorbance at a line near the analytical line where the element of interest does not absorb. The non-specific absorbance is then subtracted from that measured at the analytical line. This correction is analogous to natural color correction required in some colorimetric methods.

APPARATUS

1. Methods outlined require a Perkin Elmer Model 403 atomic absorption spectrophotometer or equivalent instrument having:

   A. Double beam optics
   B. Premix burner
   C. Optical response 180 to 900 nm
   D. Digitized readout in absorbance or concentration
   E. Time integrating, signal averaging circuitry
   F. Emission and absorbance operation modes
   G. Scaling amplifier to give readout in concentration units
   H. Curvature correction circuitry
   I. Analog and digital recorder output.

2. Hollow cathod lamps, single or multi-element type, for each element of interest.

REAGENTS

See element of interest.

PROCEDURE

With instrument settings as listed under individual metals (See Note):

1. Prepare blanks and standards to cover the concentration range of samples to be analyzed.

2. Aspirate blank solution for 10 seconds and set zero.

3. Aspirate lowest standard concentration and adjust "Concentration" potentiometer to obtain desired digital display.

4. Aspirate successively higher standards until deviation from linearity is observed. Use "Onset" to bring first deviant point into line.

5. Aspirate remaining standards and use "Magnitude" potentiometer to correct deviation.

6. Repeat aspiration of standards to check linearity of response.

7. Aspirate samples and record readings.

8. Repeat standards after samples to check machine stability.

CALCULATIONS

None required unless samples are diluted. With equipment described readout is in concentration.

NOTE

Instrument settings listed with individual elements are only

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average settings. For peak performance of a particular
instrument, these will doubtless be different.

SELECTED REFERENCE

Christian, G.D.,and F.J. Feldman.   1970.   Atomic
absorption spectroscopy: applications in agriculture,
biology and medicine. John Wiley & Sons, Inc., New
York, N.Y. 490 p.

CALCIUM BY ATOMIC ABSORPTION

PRECISION

Level	-	2.5 mg Ca/liter
Standard deviation	-	±0.03 mg Ca/liter

OPERATING RANGE

- Light path through length of flame 0.01-12 mg Ca/l.
- Light path through width of flame 0.1-200 mg Ca/l.

INSTRUMENT SETTINGS   - For Perkin Elmer Model 403.

Wavelength	-	423 nm
UV or Visible	-	Visible
Slit	-	4
Emission chopper	-	Off
Filter	-	Out
Readout mode	-	"Concentration" "Repeat"
Signal conditioning	-	10 average
Recorder response	-	1
Fuel - Acetylene	-	28 units
Oxidant - Air	-	37 units
Burner Height	-	8.0 units

INTERFERENCE

Calcium absorption is subject to chemical interference from a number of sources. In freshwater the most significant of these are silicate, phosphate and carbonate which in the flame form refractory compounds with calcium, yielding low estimates. Most suppressing interferences can be overcome by adding about 1% lanthanum chloride or 0.5% strontium chloride.

REAGENTS

A.   Lanthanum chloride buffer

Lanthanum oxide	58.65	g
Hydrochloric acid	250	ml

Wet lanthanum oxide with 100 ml of distilled water.
Add hydrochloric acid very slowly while stirring. Cool
and make to 1 liter with distilled water.

B.   Calcium standard

Dissolve 2.497 g calcium carbonate in a minimum of
1 N HCl and make to 1 liter with distilled water.

1.00 ml = 1.00 mg Ca

Commercially prepared standards are acceptable.

PROCEDURE

1.   Prepare calcium standards to cover the range of sample
     concentrations.

2.   Add lanthanum chloride solution to blanks, standards, and
     samples in the ratio 1 part lanthanum solution plus 4 parts
     sample. The absolute ratio is not critical; it is, however,
     very important that the ratio used be the same for standards
     and samples.

3.   Aspirate lanthanum blank and zero instrument.

4.   Aspirate standards to calibrate instrument and adjust
     curvature.

5.   Aspirate samples and record digital display when stable.

SELECTED REFERENCE

Perkin Elmer Methods Manual.

IRON BY ATOMIC ABSORPTION

PRECISION

Level	-	0.52 mg Fe/liter
Standard deviation	-	±0.03 mg Fe/liter

OPERATING RANGE

- Light path through length of flame 0.04-10 mg Fe/liter.
- Light path through width of flame 0.4-100 mg Fe/liter.

INSTRUMENT SETTINGS   - For Perkin Elmer Model 403.

Wavelength	-	249 nm
UV or Visible	-	UV
Slit	-	4
Emission Chopper	-	Off
Filter	-	Out
Readout Mode	-	"Concentration" "Repeat"
Signal Conditioning	-	10 Average
Recorder Response	-	1
Fuel - Acetylene	-	28 units
Oxidant - Air	-	37 units
Burner Height	-	8 units

REAGENTS

A.   Iron standard

A commercial prepared standard is used, having a concentration of 1 g Fe/liter

1.00 ml = 1 mg Fe

PROCEDURE

1.   Prepare iron standards to cover the range of sample concentrations.

2. Aspirate a distilled water blank and zero instrument.

3. Aspirate standards to calibrate instrument and adjust curvature (see general AAS outline).

4. Aspirate sample and record digital display when stable.

SELECTED REFERENCE

Perkin Elmer Methods Manual.

MAGNESIUM BY ATOMIC ABSORPTION

PRECISION

Level	- 0.80 mg Mg/liter
Standard deviation	- ±0.02 mg Mg/liter

OPERATING RANGE

- Light path through length of flame 0.005-5 mg Mg/l.
- Light path through width of flame 0.5-50 mg Mg/l.

INSTRUMENT SETTINGS

- For Perkin Elmer Model 403.

Wavelength	- 285 nm
UV or Visible	- UV
Slit	- 5
Emission Chopper	- Off
Filter	- Out
Readout Mode	- "Concentration" "Repeat"
Signal Conditioning	- 10 Average
Recorder Response	- 1
Fuel - Acetylene	- 28 units
Oxidant - Air	- 37 units
Burner Height	- 8 units

INTERFERENCES

Magnesium absorption is subject to several chemical interferences. In freshwater the most significant of these are phosphate and silicate which in the flame form refractory compounds with magnesium. Addition of 1% lanthanum chloride or 0.5% strontium chloride to samples overcomes these interferences.

REAGENTS

A. Lanthanum chloride buffer

Lanthanum oxide	58.65	g
Hydrochloric acid	250	ml

Wet lanthanum oxide with 100 ml of distilled water.
Add hydrochloric acid very slowly with stirring.
Cool and make to 1 liter with distilled water.

B.   Magnesium standard

Dissolve 3.469 g magnesium carbonate in a minimum of
1 N HCl and make to 1 liter with distilled water.

$$1.00 \text{ ml} = 1.00 \text{ mg Mg}$$

Commercially prepared standards are acceptable.

PROCEDURE

1.   Prepare magnesium standards to cover the range of sample concentrations.

2.   Add lanthanum chloride solution to blanks, standards, and samples in the ratio 1 part lanthanum solution plus 4 parts sample. While the absolute ratio is not critical it is very important that the ratio be the same for standards and samples.

3.   Aspirate blank and zero instrument.

4.   Aspirate standards to calibrate instrument and adjust curvature (see general AAS outline).

5.   Aspirate samples and record digital display when stable.

SELECTED REFERENCE

Perkin Elmer Methods Manual.

MANGANESE BY ATOMIC ABSORPTION

PRECISION

Level	- 1.00 mg Mn/liter
Standard deviation	- ±0.01 mg Mn/liter

OPERATING RANGE

- Light path through length of flame 0.01-10 mg Mn/1.
- Light path through width of flame 0.1-100 mg Mn/1.

INSTRUMENT SETTINGS

- For Perkin Elmer Model 403.

Wavelength	- 279 nm
UV or Visible	- UV
Slit	- 4
Emission Chopper	- Off
Filter	- Out
Readout Mode	- "Concentration" "Repeat"
Signal Conditioning	- 10 Average
Recorder Response	- 1
Fuel - Acetylene	- 28 units
Oxidant - Air	- 37 units
Burner Height	- 8 units

REAGENTS

A.   Manganese standard

Dissolve 3.076 g manganous sulphate monohydrate in distilled water and make up to 1 liter.

1.00 ml = 1.00 mg Mn

Commercially prepared standards are acceptable.

PROCEDURE

1.   Prepare manganese standards to cover the range of sample concentrations.

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2. Aspirate distilled water blank and zero instrument.

3. Aspirate standards to calibrate instrument and adjust curvature (see general AAS outline).

4. Aspirate sample and record digital display when stable.

SELECTED REFERENCE

Perkin Elmer Methods Manual.

POTASSIUM BY ATOMIC ABSORPTION (LOW LEVEL)

PRECISION

    Level   - 0.33 mg K/liter

    Standard deviation   - ±0.01 mg K/liter

OPERATING RANGE   - Light path through length of flame 0.03-2 mg K/liter.

INSTRUMENT SETTINGS   - For Perkin Elmer Model 403.

    Wavelength   - 769.9 nm
    UV or Visible   - Visible
    Slit   - 4
    Emission Chopper   - Off
    Filter   - In
    Readout Mode   - "Absorbance" "Repeat"
    Signal Conditioning   - 100 Average
    Recorder Response   - 1
    Fuel - Propane   - 15 units
    Oxidant - Air   - 28 units
    Burner Height   - 4 units

INTERFERENCES

Ionization of alkali metals is negligible in the air-propane flame. The presence of sodium in the sample will not cause any interference.

REAGENTS

A.   Potassium standard

        Dissolve 1.907 g potassium chloride in distilled water and make to 1 liter.

                 1.00 ml = 1.00 mg K

        Commercially prepared standards are acceptable.

PROCEDURE

1. Prepare potassium standards to cover the operating range.

2. Aspirate distilled water blank and zero instrument.

3. Aspirate one standard and adjust fuel-air ratio to maximize absorbance. This step is important since absorbance is strongly dependent on fuel-air ratio for the air-propane flame.

4. Aspirate distilled water blank and zero instrument again.

5. Aspirate standards and samples and record absorbance values.

CALCULATIONS

1. Prepare a standard curve and calculate a unit absorbance factor. Over the operating range the standard curve should be linear.

$$\text{Unit absorbance factor} = \frac{\text{Standard concentration (mg K/l)}}{\text{Absorbance}}$$

2. Concentration of potassium in samples is obtained by multiplying sample absorbance value by unit absorbance factor.

SELECTED REFERENCES

Analytical methods for flame spectroscopy. Varian Techtron.

Slavin, W. 1968. Atomic absorption spectroscopy. Interscience publishers, a division of John Wiley and Sons, Inc., New York, N.Y. 302 pp.

POTASSIUM BY ATOMIC EMISSION

PRECISION

Level	- 5.0 mg K/liter
Standard deviation	- ±0.16 mg K/liter

OPERATING RANGE

- Light path through length of flame 0.05-10 mg K/l.
- Light path through width of flame 0.5-50 mg K/l.

INSTRUMENT SETTINGS

- For Perkin Elmer Model 403.

Wavelength	- 766.5 nm
UV or Visible	- Visible
Slit	- 4
Emission Chopper	- On
Filter	- In
Readout Mode	- "Intensity" "Repeat"
Signal Conditioning	- 10 Average
Recorder Response	- 1
Fuel - Acetylene	- 28 units
Oxidant - Air	- 37 units
Burner Height	- 8 units

INTERFERENCES

Ionization interference from proportionately high concentrations of sodium is possible in some samples. This interference enhances observed potassium levels but can be eliminated by preparing potassium standards containing sodium at the same level as samples.

REAGENTS

A.   Potassium standard

Dissolve 1.907 g potassium chloride in distilled water and make to 1 liter.

$$1.00 \text{ ml} = 1.00 \text{ mg K}$$

Commercially prepared standards are acceptable.

PROCEDURE

1. With instrument settings as listed use a potassium hollow cathode lamp to adjust the monochromator to the principle emission line at 766.5 nm (383 on monochromator dial). Remove lamp.

2. Aspirate distilled water blank and zero instrument.

3. Aspirate standards and adjust concentration dial to give required readout. In "Intensity" mode the "onset" and "magnitude" potentiometers have no effect. If the calibration curve is non-linear this can be remedied by careful adjustment of ratio of flame gases and burner height.

4. Aspirate samples and record digital display when stable.

SELECTED REFERENCE

Perkin Elmer Methods Manual.

SODIUM BY ATOMIC ABSORPTION

PRECISION

Level	-	4.80 mg Na/liter
Standard deviation	-	±0.2 mg Na/liter

OPERATING RANGE
- Light path through length of flame 0.01-5 mg Na/1.
- Light path through width of flame 0.05-50 mg Na/1.

INSTRUMENT SETTINGS
- For Perkin Elmer Model 403.

Wavelength	-	590 nm
UV or Visible	-	Visible
Slit	-	3
Emission Chopper	-	Off
Filter	-	Out
Readout Mode	-	"Concentration" "Repeat"
Signal Conditioning	-	10 Average
Recorder Response	-	1
Fuel - Acetylene	-	28 units
Oxidant - Air	-	37 units
Burner Height	-	8 units

INTERFERENCES

There appear to be no significant interferences for sodium determination in freshwater.

REAGENTS

A. Sodium standard

Dissolve 2.542 g sodium chloride in distilled water and make to 1 liter.

1.00 ml = 1.00 mg Na

Commercially prepared standards are acceptable.

PROCEDURE

1. Prepare sodium standards to cover the range of sample concentration.

2. Aspirate distilled water blank and zero instrument.

3. Aspirate standards to calibrate instrument and adjust curvature (see general AAS outline).

4. Aspirate samples and record digital display when stable.

SELECTED REFERENCE

Perkin Elmer Methods Manual.

SPECIFIC CONDUCTANCE

PRECISION

    Level   - 150 μS/cm

    Standard deviation   - ±0.01 μS/cm

OPERATING RANGE   - This is dependent on the instrument used and the cell constant of electrode.

                               Cell constant = 0.1 cm^{-1} (0.1 μS-150 mS)
                               Cell constant = 1.0 cm^{-1} (1 μS-1500 mS)

SAMPLE CONDITION   - Unfiltered.
                        - Stored at 5 C less than 30 days.

METHOD PRINCIPLE

Solutions of dissociated ions can conduct electrical current. The resistance (R) of electrolyte solutions is a function of electrode surface area (A), distance between electrodes (ℓ), solution temperature, and the concentration and nature of ion in solution. For given solution and temperature:

$$R(ohms) \quad \propto \quad \frac{\ell(cm)}{A(cm^2)} \qquad (1)$$

Resistance is measured with platinum electrodes (coated with platinum black) using a bridge circuit with an alternating current supply at 60-3000 Hz to minimize polarization effects. Under these conditions Ohm's law is obeyed.

A more commonly used measurement than resistance is conductance (L) measured in Siemens (S) where:

$$L(Siemens) \quad = \quad \frac{1}{R(ohms)} \qquad (2)$$

From equations (1) and (2) then

$$L \quad \propto \quad \frac{A}{\ell} \qquad\qquad (3)$$

or

$$L = K \left(\frac{A}{\ell}\right) \qquad\qquad (4)$$

where K is a proportionality constant termed the specific conductance and is the observed conductance of a solution measured with a cell of unspecified geometry (A and ℓ) normalized to the conductance one would obtain with a cell having $A = 1\,cm^2$ and $\ell = 1$ cm. K is usually measured at 25 C.

$$\text{From (4)} \quad K\ (S/cm) = \frac{\ell\ (cm)}{A\ (cm^2)} \cdot L(Siemens) \qquad\qquad (5)$$

$\frac{\ell}{A}$ is termed the cell constant which varies with the geometry of the cell used (area of electrode plates, and their separation ℓ). Commercially prepared cells are labelled with an approximate cell constant but must be calibrated before use by measuring the conductance L of a KCl solution of known specific conductance K at 25 C and calculating ℓ/A from equation (5). Specific conductance of samples is obtained by measuring L for samples at 25 C and calculating using equation (5) and the calibrated cell constant.

REAGENTS

A.　Distilled and deionized water - Specific conductance (25 C) not to exceed 10 µS/cm.

　　　This can be prepared by passing distilled water through a mixed bed ion exchange resin.

B.　Potassium chloride - 0.2 N

　　　Dissolve 14.912 g of dry KCl in distilled and deionized water and make to 1 liter.

C,　Potassium chloride $\div$ 0.01 N

　　　Dilute 50.0 ml of 0.2 N KCl to 1 liter with distilled water.

Specific conductance (25 C) = 1411 µS/cm (see Kortum et al.).

APPARATUS

1. YSI Model 31 conductivity bridge or equivalent.

2. YSI conductivity cell #3403.

    Cell constant $\simeq 1.0$ cm^{-1}.

3. Water bath to maintain samples at 25 ± 1 C.

PROCEDURE

1. Place 3 portions of 0.01 N KCl and samples in water bath (standards and samples are usually in 500 ml polyethylene bottles). Allow standards and samples to come to 25 C.

2. Measure conductance of standards (L_{KCl}) and samples (L_s) rinsing the electrode with distilled and deionized water between readings.

CALCULATIONS

1. Calculate the conductivity cell constant

    from (5) Cell Constant $= \dfrac{1411}{L_{KCl}}$

    where 1411 is the accepted specific conductance of a 0.01 N KCl solution at 25 C and L_{KCl} is the observed conductance of a 0.01 N KCl solution at 25 C.

2. Multiply all sample conductance readings (L_s) by the cell constant obtained above to give specific conductance values for samples.

SELECTED REFERENCES

Barrow, G.M. 1966. Physical chemistry. McGraw-Hill, New York, N.Y. p. 843.

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Kortum, G. and J.O!M. Bockris. 1951. Textbook of
    electrochemistry. Vol, 1. Elsevier Press, Inc.,
    Houston, Texas. p. 209.

CHLOROPHYLL a (FLUOROMETRIC METHOD)

PRECISION

    Level   - 1.2 µg chlorophyll a/liter

    Standard deviation   - 0.12 µg chlorophyll a/liter

OPERATING RANGE   - Depends on volume of liquid available or capable of being filtered. Minimum detectable quantity of chlorophyll a in 10 ml of 90% acetone ranges from 0.01-0.05 µg depending on the individual instrument used.

SAMPLE CONDITION   - Stored at 5 C less than 48 hours.
                                 - Do not acidify or freeze water samples.
                                 - Particulate collected on Whatman GF/C 4.25 cm glass fiber filters. Filters can be frozen and stored in dark indefinitely.

METHOD PRINCIPLE   - Particulate matter collected on a glass fiber paper is ground in acetone. Plant pigments appear to be quantitatively extracted. The extract is filtered.

                                      For chlorophyll a, excitation between 430-450 nm gives an emission maximum between 650 and 675 nm. In the method described a fluorometer, equipped to provide excitation around 440 nm, and detect emission at around 660 nm is used. The output of the instrument is in arbitrary units and it must be calibrated using a chlorophyll a solution of known concentration.

                                      Since pure chlorophylls are not easily obtained one must prepare a stock chlorophyll solution and standardize

it. Lettuce leaf is a convenient source; it is neutral, low in chlorophyllase, and obtainable year round.

With the fluorometer settings recommended, the instrument responds almost exclusively to chlorophyll a. However, chlorophyll degradation products will also produce a response and when present (as may be the case with samples from aphotic waters or sediments) this method will over-estimate chlorophyll a.

REAGENTS

A. Acetone 90% v/v

Mix 900 ml of acetone (acid free) with 100 ml of distilled water. Acid free acetone can be prepared by distillation over magnesium carbonate.

B. Chlorophyll stock solution

Using 90% acetone, extract about 5 cm^2 green lettuce leaf to obtain 25 ml of chlorophyll solution which is deep green in colour. Filter and store in the dark at 5 C.

APPARATUS

1. Tissue grinder - 15 ml volume

Scientific Glass Apparatus Co. Inc. #JT-4110 or equivalent. These tissue grinders are designed for manual use but can be modified so that the pestle can be driven with a 1/4" electric drill. The glass handle on the pestle is cut off and a stainless steel shaft inserted down into the hollow pestle and fixed in place with epoxy cement.

2. Electric drill - 1/4" - variable speed

3. Filtration assembly - All glass, small surface area (Figure 25).

ALL GLASS FILTRATION ASSEMBLY

(A) GLASS FUNNEL-50 ml.

(B) GLASS FIBER FILTER

(C) SINTERED GLASS FILTER SUPPORT WITH GROUND GLASS FITTING

(D) GLASS ADAPTER WITH SIDE ARM TO VACUUM AND GROUND GLASS FITTINGS

(E) 10 ml. GRADUATED CYLINDER
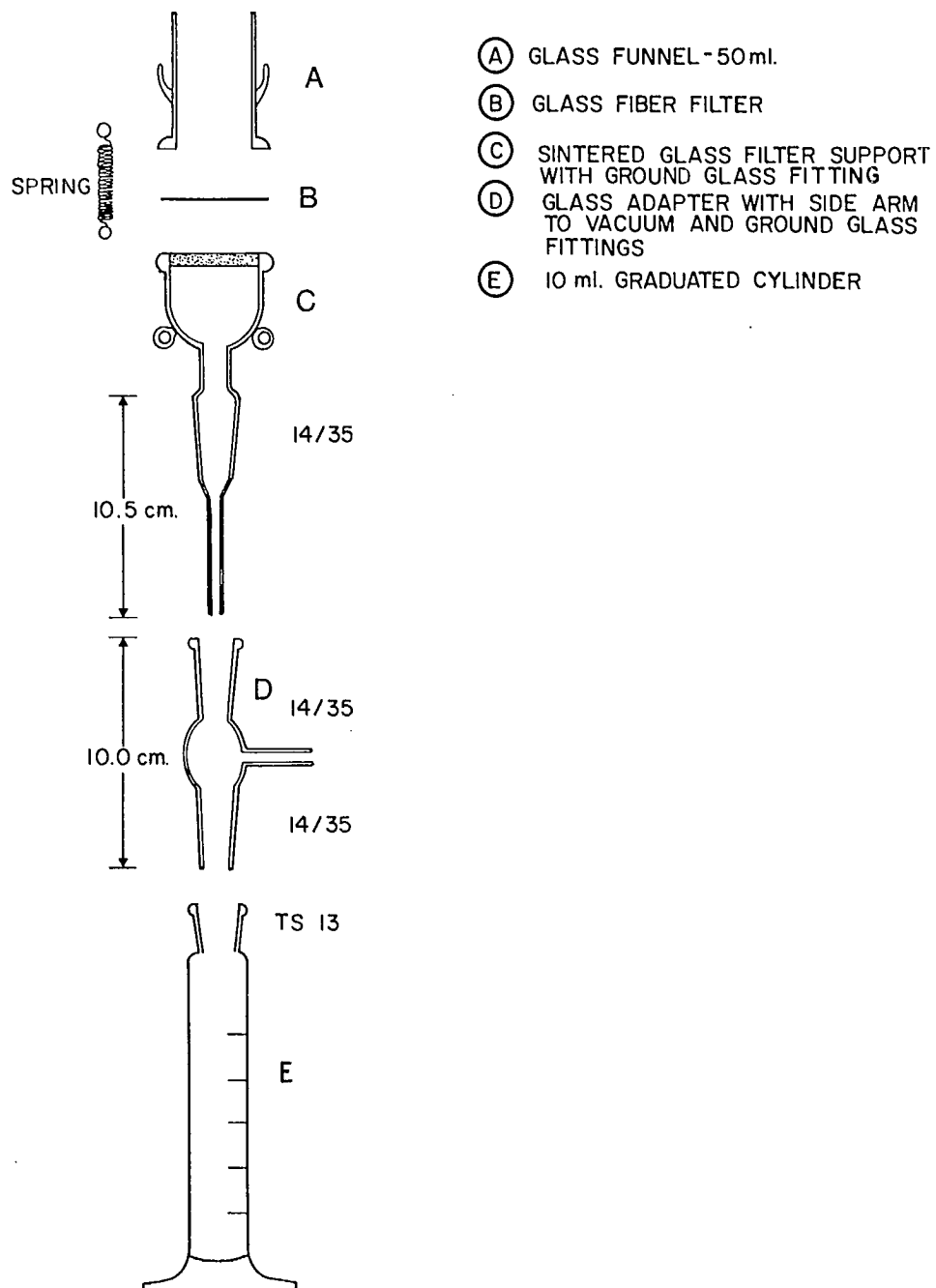
FIGURE 25.

4.   Turner Model III Fluorometer equipped with:

      A.   Primary filter - Kodak Wratten No. 47B
      B.   Secondary filter - Corning 2-64
      C.   Blue source lamp - Turner No. 110-853
      D.   Door with standard cuvette holder

5.   Spectrophotometer to calibrate the chlorophyll stock
solution. A scanning model is to be preferred but is not
essential.   Spectrophotometer should be checked for
accuracy of wavelength settings.

PROCEDURE

Standardization of chlorophyll solution.

1.   Dilute the stock solution if necessary, so that E_{1cm}^{665nm} is
approximately 0.6, corresponding to about 6 mg chlorophyll
a/l.

2.   In a spectrophotometer measure absorbances, in 1 cm cuvettes,
of the above solution and of 90% acetone, at 665, 645 and 750 nm
using 90% acetone in the reference path.

3.   Correct the chlorophyll readings, first, by subtracting those
of 90% acetone, at the 3 wavelengths. This corrects for
differences between cuvettes. Then, from the corrected
readings at 665 and 645, subtract the corrected reading at
750 nm, to give readings E_{1cm}^{665nm} and E_{1cm}^{645nm}. This second
subtraction, which should be small, corrects for any non-
chlorophyll absorption in the solution.

4.   Calculate chlorophyll a concentration (mg/l) from

$$C = 11.57 \ E_{1cm}^{665nm} - 1.35 \ E_{1cm}^{645nm}$$

This equation is derived from that of Parsons and Strickland
(1963), on the assumption that only chlorophylls a and b are
present in lettuce. Similar results are obtained from
the more recent SCOR-UNESCO factors. For this, the wave-
lengths are 663, 645 and 750 nm, and the equation should be

$$C = 11.66 \ E_{1cm}^{663nm} - 2.14 \ E_{1cm}^{645nm}$$

Calibration of fluorometer.

1. Using the standard solution calibrated above, prepare
    accurate dilutions with 90% acetone so that at least 3
    readings are obtained on each sensitivity setting. If
    possible the readings should come at approximately 25, 50,
    and 75 divisions. Several of these dilutions can be used
    to obtain readings on more than one sensitivity setting.

2. Plot scale reading against chlorophyll a concentration (μg/1)
    in acetone, for each sensitivity setting. From the graphs
    obtain a scale factor (slope) for each sensitivity setting.

$$\text{i.e.} \quad F_{(1x,3x,10x,30x)} = \frac{\text{Chlorophyll } a\,(\mu g/1)}{\text{Scale Reading}}$$

These plots should be linear. On some fluorometers the plot
for the 1x setting may show some curvature at higher
readings. If this is the case this setting should not be
used at readings higher than those of the linear portion
of the plot.

3. The fluorometer need only be calibrated before its initial
    use. However it should be checked at least once a year and
    it must be recalibrated if any maintenance or repairs are
    performed.

ANALYSIS OF SAMPLES

1. Mix water sample well and measure an appropriate volume (V_1)
    into a graduated cylinder and collect particulate on a glass
    fiber filter. Vacuum should not exceed 15 inches of Hg.

2. If filters are not to be processed immediately, store in the
    dark at -10 C.

3. Place filter paper in tissue grinder with 2-3 ml of 90%
    acetone.

4. Grind for 1 minute taking care not to lose any of the
    solvent through splashing.

5. Transfer the paper and acetone slurry to an all-glass
    filtration assembly using 2-3 ml of 90% acetone to rinse out
    the tissue grinder. Collect acetone filtrate in a 10 ml
    graduated cylinder.

6. Wash the filter assembly with 2-3 ml of acetone.

7. Make the acetone extract up to 10 ml or appropriate volume (V_2).

8. Zero fluorometer using 90% acetone.

9. Measure fluorescence to nearest 0.2 units using appropriate sensitivity setting. Extracts that are off scale on the lowest sensitivity setting should be diluted with 90% acetone.

NOTE

It is essential that the time from extraction to measurement of fluorescence be short with minimum exposure to light. We have found extracted pigments to be quite stable at room temperature if maintained in total darkness.

CALCULATIONS

1. Chlorophyll a concentrations ($\mu g/l$) in the original water sample can be obtained from the following equation:

$$\text{Chlorophyll } a \text{ } (\mu g/\text{liter}) = F \times \text{(fluorometer reading)} \times \left(\frac{1000}{V_1}\right) \times \left(\frac{V_2}{1000}\right)$$

where V_1 (ml) is the volume of water filtered and V_2 (ml) is the volume of 90% acetone into which chlorophyll a is extracted.

SELECTED REFERENCES

Parsons, T.R., and J.D.H. Strickland. 1963. Discussion of spectrophotometric determination of marine plant pigments, with revised equations for ascertaining chlorophylls and carotenoids. J. Mar. Res. 21:155-163.

UNESCO. 1966. Determination of photosynthetic pigments in sea water. Unesco, Paris. 69 p.

Yentsch, C.S. and D.W. Menzel. 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. Deep Sea Res. 10:221-31.

Strickland, J.D.H., and T.R. Parsons. 1968. A practical handbook of seawater analysis. Bull. Fish. Res. Board Can. 167:311 p.

DISSOLVED OXYGEN

PRECISION

  Level   - 10.0 mg O_2/liter

   Standard deviation - ±0.2 mg O_2/liter

OPERATING RANGE   - 0-20 mg O_2/liter

SAMPLE CONDITION

- Sampling technique is critical for this method - see section on sampling methods.
- Sample is collected in specially designed glass bottles having a capacity of 300 ml and ground glass stoppers with conical ends to prevent trapping air bubbles.
- Sample must be collected without exposure to atmosphere.
- Stored in sealed bottle at temperature sampled.
- Less than 1 hour old.
- Free of chemical reductants and oxidants (other than oxygen).

METHOD PRINCIPLE

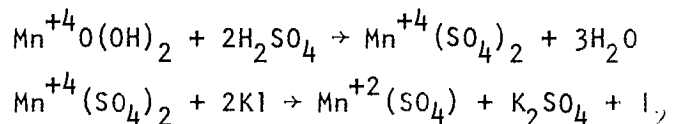- Manganous sulphate reacts with potassium or sodium hydroxide to give a white precipitate of manganous hydroxide. In the presence of oxygen, brown manganic basic oxide is formed,

i.e. $Mn^{+2}SO_4 + 2\ KOH \rightarrow Mn^{+2}(OH)_2 + K_2SO_4$

$2Mn^{+2}(OH)_2 + O_2 \rightarrow 2Mn^{+4}O(OH)_2$
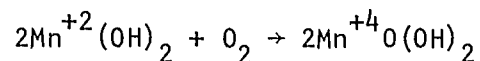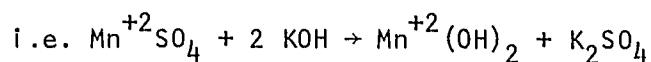
Addition of sulphuric acid dissolves the brown manganic oxide yielding manganic sulphate which reacts instantly

with iodide to yield iodine.   i.e.

$$Mn^{+4}O(OH)_2 + 2H_2SO_4 \rightarrow Mn^{+4}(SO_4)_2 + 3H_2O$$

$$Mn^{+4}(SO_4)_2 + 2KI \rightarrow Mn^{+2}(SO_4) + K_2SO_4 + I_2$$

In effect, oxygen oxidizes Mn^{+2} to Mn^{+4} and Mn^{+4} oxidizes I^- to I_2. Iodine is then determined titrimetrically with starch as an end point indicator.

Interferences occur from other oxidants in the sample which will liberate iodine. The effect of nitrite is eliminated with the addition of sodium azide.

REAGENTS

A.   Manganese sulphate

Dissolve 480 g of $MnSO_4 \cdot 4H_2O$, 400 g of $MnSO_4 \cdot 2H_2O$, or 364 g $MnSO_4 \cdot H_2O$ in distilled water. Filter and dilute to 1 liter.

B.   Alkaline iodide azide

Dissolve 500 g sodium hydroxide, or 700 g potassium hydroxide, and 135 g sodium iodide, or 150 g potassium iodide, in distilled water and dilute to 1 liter. To this add 10 g sodium azide dissolved in 40 ml of distilled water.

C.   Sulphuric acid

Concentrated (S.G. 1.84).

D.   Starch indicator

Bring 100 ml distilled water to boiling. Prepare a paste of 1 g of potato starch in a few ml of distilled water. Add the boiling water to the paste. Cool and store at 5 C. When a violet or grey tinge is noted discard.

E.   Sodium thiosulphate

Prepared from commercially available concentrated
standard solutions. Dilute concentrated standard to
0.025 N with distilled water. Prepare fresh weekly.
Store at 5 C. Bring to room temperature before using.

APPARATUS

1. Dissolved oxygen bottles to contain 300 ml. These must be
    calibrated (to the nearest ml) if second decimal place
    accuracy is necessary.

2. Dispensing pipettes to deliver 2 ml. - One for each of:
    manganese sulphate reagent (A), alkaline iodide reagent
    (B), and sulphuric acid (C). It is important that each
    pipette is used for only one reagent and that the caps for
    the reagent bottles are not mixed up.

3. Burette - Type used depends on accuracy required and levels
    to be measured.

4. Magnetic stirring plate with light source in base.

5. 200 ml pipette.

PROCEDURE

1. To the water sample in a calibrated dissolved oxygen bottle
    add 2 ml of manganese sulphate reagent (A) followed by 2 ml
    of alkaline-iodide-azide reagent (B). These reagents should
    be injected well below the liquid surface with sample
    bottles being open for as short a time as possible.

2. Re-stopper the bottle taking care not to entrap air bubbles,
    and agitate vigorously to mix reagents.

3. When the precipitate has settled to the bottom a second time,
    remove the stopper and inject 2 ml of sulphuric acid (C).
    Re-stopper the bottle and mix gently.

    It is essential in the above manipulations that none of the
    precipitate, or iodine arising from acidification of the
    precipitate, escapes from the bottle.

5. Remove 200.0 ml of solution from the bottle and add to a 250 ml Erlenmeyer flask.

6. If the colour of the sample indicates much iodine present (deep orange) begin titrating the sample with 0.025 N thiosulphate (E) until colour intensity is reduced to a pale straw yellow colour. Add several drops of starch solution and titrate until first disappearance of the blue colour.

7. If the colour of the sample is pale yellow to begin with, add starch indicator before beginning titration.

CALCULATIONS

A. 1.0 ml of 0.025 N thiosulphate is equivalent to 25×10^{-6} equivalents of iodine which is in turn equivalent to 25×10^{-6} equivalents of oxygen.

$$25 \times 10^{-6} \text{ equivalents of } O_2 = 200 \times 10^{-6} \text{ g } O_2$$

If volume titrated is 200 ml then 1.0 ml of 0.025 N thiosulphate titrant is equivalent to 1.0 mg O_2/liter in the original sample.

If oxygen concentrations to 0.1 mg/liter are acceptable, the above equality is sufficient to determine dissolved oxygen.

B. If greater accuracy is required one must take into account the dilution effect of the first two reagent additions. This dilution effect is $\frac{V-4}{V}$ where V is the volume in ml of the oxygen bottle used. Oxygen values obtained by assuming 1.00 ml of 0.025 N thiosulphate equivalent to 1.00 mg/liter dissolved oxygen should then be multiplied by $\frac{V}{V-4}$ to correct for dilution.

SELECTED REFERENCES

American Public Health Association. 1965. Standard methods for the examination of water and waste water. 12th ed. APHA, New York, N.Y. 769 p.

TOTAL DISSOLVED SOLIDS - (TDS)

PRECISION

    Level   - 46 mg/liter

    Standard deviation   - ±4 mg/liter

OPERATING RANGE   - 10 mg/liter to saturation level of salts present.

SAMPLE CONDITION   - Stored at 5 C.
                               - Less than 30 days old.
                               - Filter through Whatman GF/C.

METHOD PRINCIPLE   - A known volume of water (usually 100 ml) is placed in a pre-weighted evaporating dish and evaporated without boiling. The solid residue is determined by re-weighing the evaporating dish. Since a number of elements form salts which crystallize as hydrates (over-estimate of TDS), or salts which decompose and lose weight during evaporation (under-estimate), this test is of empirical value only and does not correctly measure the weight of dissolved salts present. In waters with specific conductance less than 100 μS/cm weighing errors are significant and TDS values become meaningless unless special precautions are taken.

APPARATUS

1.   Glass evaporating dishes to contain 100 ml.

2.   Oven or infra-red heat lamps to evaporate water samples. Temperature should be just above 100 C.

3. Add 100.0 ml of filtered sample to each dish.

4. Place samples in oven at 104 C for 16 hours.

5. Cool dishes in desiccator and re-weigh.

CALCULATIONS

1. Subtract final weight from tare weight and express as mg of dissolved solids.

2. Multiply the above weight by 10 to yield dissolved solids in mg/liter.

SELECTED REFERENCE

American Public Health Association. 1965. Standard methods for the examination of water and waste water. 12 th ed. APHA. New York, N.Y. 769 p.

HYDROGEN ION CONCENTRATION - pH

PRECISION

Level	- 8.49
Standard deviation	- ±0.02

OPERATING RANGE - 1-14 pH units

SAMPLE CONDITION

- Unfiltered, stored at 5 C.
- Less than 24 hours old.
- Sample brought to room temperature before analysis.

METHOD PRINCIPLE

The pH of an aqueous solution is defined operationally by the following equation:

$$pH = pHs + \frac{(E-E_s)}{0.000198\ T}$$

where pHs is the assigned pH of a buffer used to standardize the system. E and E_s are the EMF's of a suitable cell arrangement with unknown and buffer respectively and T is the temperature (Kelvin). Usually the cell arrangement consists of a glass electrode with an electrolyte bridge to a saturated calomel electrode. Cell EMF is measured with a high impedance voltmeter with usual response being 59 mV per pH unit at 25 C.

The glass electrode assembly is fragile and requires careful use and frequent calibration to obtain meaningful results. Since electrode response may be non-linear it is important to standardize using buffers having a pH close to and preferably bracketing the pH of samples. Suitable time must be allowed for the electrode to come to equilibrium with solutions before a reading is taken. Care must be taken to avoid electrostatic effects such as occur when using Teflon[R] or polypropylene laboratory ware, or from nylon clothing worn by the analyst.

REAGENTS

A. Standard buffer solutions

Commercially prepared - to cover range of pH to be measured.

APPARATUS

1. Glass electrode.

2. Calomel reference electrode.

3. Combination electrode (combines 1 and 2 above in a single probe. Either 1 and 2, or 3 are required.).

4. pH meter - Orion Model 801 or other instrument suitable for needs.

PROCEDURE

1. Turn on pH meter and allow to warm up.

2. Be sure electrodes have been pre-soaked according to manufacturer's specifications and that reference electrode is filled.

3. Place electrodes in appropriate buffer, measure buffer temperature and adjust temperature compensation on pH meter.

4. Adjust pH meter to read buffer pH level.

5. Rinse electrodes with distilled water and place in a second buffer solution, several pH units different than the first buffer solution, to check linearity of response.

6. Rinse electrodes and immerse in samples taking care to adjust temperature compensation if necessary.

7. Read pH.

CALCULATIONS

No calculations required as instrument reads directly in pH units.

PARTICULATE SOLIDS

PRECISION

Level	-	8 mg/liter
Standard deviation	-	±0.5 mg/liter

OPERATING RANGE - Depends on sample volume available or possible to filter. If possible, volume filtered should be such to give 2.5 mg suspended matter per filter paper.

SAMPLE CONDITION
- Stored at 5 C.
- Less than 48 hours old.
- Particulate collected on either Whatman GF/C (>5 mq/liter) or Millipore^R matched pair filters (<5 mg/liter).

METHOD PRINCIPLE

Particulate material from a sample is collected on a pre-weighed filter, the pore size of which determines what is considered "Suspended Solids". Particulate and paper are dried and re-weighed, the increase in weight being attributed to suspended solids.

For low levels of suspended matter the fact that a finite amount of sample water (plus its dissolved solids content) remains in the paper and the fact that part of the filter paper may be solubilized or abraded away in the filtration process, necessitates special precautions. These effects can best be overcome using matched weight filter paper pairs (Millipore^R AAWP0470W). These papers are guaranteed to be within 0.1 mg of each other and are placed in tandem in the filtration assembly. The second paper is used as the tare for the first.

APPARATUS

1. Drying oven set at 104 C.

2. Whatman GF/C 4.25 cm filter papers or Millipore[R] (AAWP0470W) matched pair filters.

3. Millipore[R] filtration assembly.

PROCEDURE

1. Dry filter papers at 104 C for 1 hour. (Only GF/C papers require this step.)

2. Weigh filters to the nearest 0.1 mg. (Only GF/C papers require this step.)

3. Agitate sample and measure suitable volume into a graduated cylinder. Collect particulate on filter with a vacuum of less than 15 inches of Hg.

4. Dry filter papers 1 hour at 104 C.

5. Re-weigh papers plus particulate to the nearest 0.1 mg.

CALCULATIONS

1. For GF/C papers* subtract the initial weight from final weight to get weight of suspended matter on the filter. Multiply this weight (in mg) by $\dfrac{1000}{ml\ of\ sample}$ to get mg suspended solids/liter.

2. For Millipore matched pair filters use the blank paper weight for the tare value and calculate as above.

* The sample collected on this filter paper can be used for suspended phosphorus analysis.

SELECTED REFERENCES

American Public Health Association. 965. Standard methods for the examination of water and waste water. 12th ed. APHA, New York, N.Y. 769 p.

Millipore Corp. 1973. Suspended solids analysis. Application Procedure AP312.

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