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MANUSCRIPT REPORT SERIES
(OCEANOGRAPHIC and LIMNOLOGICAL)
No. 18

Standard Methods of Seawater Analyses
Volume I
A re-printing including recent addenda

by
J. D. H. Strickland

Pacific Oceanographic Group
Nanaimo, B.C.

July 15, 1958

Programmed
by
THE CANADIAN JOINT COMMITTEE ON OCEANOGRAPHY

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PREFACE TO COLLECTED STANDARD METHODS

(File N 7-1-5 July 31, 1957)

These nine methods form the core of some two dozen procedures which will eventually be released by the Pacific Oceanographic Group. Methods for nitrate and ammonia will follow shortly and it is hoped to extend the work to cover most of the metals such as iron, manganese, copper, zinc and molybdenum, known to be essential to the enzyme systems of marine life.

Trivial changes and additions will be issued from time to time as addenda to these methods. A method will be completely re-issued, under a separate letter code, if experience indicates a major revision or change of approach is merited.

These methods are intended for domestic use and limited private circulation and no discussion of or reference to the literature is included. Basic working instructions are given in full detail. Notes on the chemistry involved are only included where this knowledge can contribute materially to the speed and efficiency of the operator. Some methods are taken directly from the literature, others are based on ideas taken from more than one literature source. In many instances, the original procedures have been greatly modified, where this has been shown to result in an increase of speed, precision, or operational simplicity.

All methods have had a thorough trial under land or shipboard laboratory conditions and the precision limits of each method are calculated from a statistical treatment of the results so obtained. In most oceanographic work it is now imperative that an estimate be made of the statistical significance of any result that is obtained. The prime purpose of issuing these methods is that standardized procedures can now be used which give results having a known variance.

J. Strickland

J.D.H. Strickland,
Chemist.

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Approved June, 1957. Standard Method No. Sal. 1.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF SALINITY BY SILVER NITRATE TITRATION

(HIGH PRECISION METHOD)

(File N 7-1-5 June 30, 1957).

Definitions

A. Chlorinity

Halogen ions in sea water are normally estimated by argentimetry. To prevent ambiguity arising from changes in the accepted atomic weights of silver and chlorine the chlorinity, Cl °/₀₀, of sea water is defined as 0.3285234 times the weight of silver precipitated as silver halides from 1 kg. of sea water, all weighings being in vacuo.

B. Salinity

The salt content of sea water is usually expressed as salinity, S °/₀₀, a convention which approximates to the weight in grams, in vacuo, of the solids obtained from 1 kg. of sea water (weighed in vacuo) when the solids have been dried to constant weight at 480° C, the organic matter oxidized and the bromide replaced by an equivalent amount of chloride. (Ocean water contains slightly more salts (halogens, carbonate and bicarbonate) than is expressed by its salinity value.) In practice, the salinity is defined in terms of chlorinity by the Knudsen equation:

$$S\ ‰ = 0.030 + 1.8050\ Cl\ ‰.$$

C. Chlorosity

This value, $Cl/l_{(t)}$, is the quantity determined by volumetric

methods and is defined in the same manner as chlorinity except that the sample unit is 1000 ml. of sea water at a stated temperature rather than 1 kg. of sea water weighed in vacuo.

A. Capabilities of the Method

Range S °/₀₀ 30 - 38

The following data are based on a statistical treatment of results obtained by skilled operators in a shore-base laboratory, using the procedure exactly as described and reporting results as a mean of two determinations on the same sample.

1. Precision at the 30 °/₀₀ Salinity Level.

The correct value lies in the range: Mean of duplicate determinations ± 0.017 °/₀₀.

Greater precision may be obtained by increasing the number of determinations. If n titrations are meaned and C_s (see Section H) is determined from ten or more titrations, the range becomes approximately $\pm \frac{0.023}{n^{1/2}}$ °/₀₀.

Reject duplicate determinations if the values for chlorosity differ by more than 0.025. If the duplicate titrations differ by less than this, take a mean value.

Note: The above statistical data apply at the 0.05 probability level, i.e., the odds are 19 to 1 in their favour. By this criterion two samples of sea

water cannot be considered to be significantly different in salinity unless the values differ by more than 0.03 °/₀₀ if the same standardization correction is used (see Section H below) or by more than 0.035 °/₀₀ if different standardizations have been employed (mean of duplicate sample titrations in both cases.)

B. Outline of Method

The halogens in a 15 ml. volume of sea water sample are determined by titration with a silver nitrate solution using a chromate end-point, the Mohr titration. The silver solution is standardized against the same volume of a sea water standard of known chlorinity, obtained from the Laboratoire Hydrographique at Copenhagen. Corrections are made to allow for temperature and density, so as to convert titration values to chlorinity, from which salinity values are obtained. Special Knudsen-type automatic pipettes and burettes are used.

C. Special Apparatus and Equipment

The special Knudsen-type automatic pipette and burette designed for this determination must be used. Arrangements are made for vacuum to suck samples into the pipette and for pressure to fill the burette from a large reservoir of silver nitrate. The titration is conducted in a 200 ml. tall-form beaker with rapid mechanical stirring. An automatic dispenser of diluting solution, containing the chromate indicator, is advantageous. Centigrade thermometers, read to the nearest tenth of a degree, are used to measure the temperature of the silver nitrate solution and the sea water samples immediately prior to or after a titration. The titration should be carried out against a white background in the "yellow" light of an electric light bulb rather than in daylight or in the light of artificial daylight lamp.

D. Special Reagents and Solutions Required

1. Standard Sea Water

The primary standard for this method must be a sample of Eau de Mer Normale with a stated Cl °/‰ value (near to 19.38) obtained from the Depot d'Eau Normale at Charlottenlund Slot, Charlottenlund, Denmark. To conserve this primary standard, it is best to prepare a large volume (10-20 liters) of a secondary standard consisting of filtered sea water (preferably collected below 50 m. in the open ocean) with a chlorinity exceeding 18 °/‰. This sample is stabilized by adding a few crystals of thymol and is then rapidly filled into sample bottles (see Section E). Every tenth bottle is opened and analysed in duplicate by the method described below using a silver nitrate solution that has been standardized by Eau de Mer Normale. The mean of ten or more such duplicates is taken as the chlorosity (20° C) of the secondary standard.

2. Silver Nitrate Solution (Approximately 0.207 N).

Dissolve 36 g. of good quality silver nitrate for each liter of final solution. Use distilled water and store the solution in a dark bottle. It is desirable to make this solution in units of at least 20-40 liters when large numbers of solutions are to be analysed. This solution will require dilution with a few per cent of water to bring it to the desired strength, as described in Section H. The solution should be well mixed in the bottle once or twice each day or prior to each batch of titrations.

3. Indicator-Diluent Solution

Dissolve 3.5 g. of analytical quality potassium chromate, K_2CrO_4, in each liter of distilled water.

E. Sampling Procedure and Sample Storage

Use standard flat 8-ounce medicinal bottles for collecting, shipping and storage of samples used for salinity determinations. The bottles manufactured for use with size no. 6 corks should be used. The corks are soaked for 30-40 seconds in melted paraffin wax and drained and dried by placing them on a wire screen. Extruded excesses of wax are removed. The bottles are rinsed thoroughly three times with the sample and then filled to the shoulder. They are sealed by forcing the waxed corks down to a few mm. below the level of the neck. A further seal should be made within a few days by dipping the neck in melted wax. No changes in salinity will then result over a period of many years.

When these bottles, or the containers of Eau de Mer Normale, are opened the salinity determination must be carried out within a few minutes. Repeat determinations on re-corked bottles should not be delayed for more than about one hour.

F. Experimental

Add 15.00 ml. of sample to a 200 ml. spoutless tall-form beaker by means of the automatic Knudsen-type pipette and add 15 ml. of indicator-diluent solution. The titration is made from a Knudsen-type automatic bulb burette, the graduations of which generally commence at about 16.7. (This burette delivers twice the volume indicated by the graduations so as to obtain an increased sensitivity.) The contents of the beaker must be vigorously stirred before and at the end-point. It is best to commence stirring after the bulb has about two-thirds emptied. About one ml. before it is judged that the end-point is reached, rinse the sides of the beaker and stirrer with a little distilled water from a wash bottle.

As the end-point approaches, the localized red precipitate formed by the silver solution will begin to spread throughout the solution. At the end-point

the pale greenish-yellow colour of the contents of the beaker changes to a full yellow and then becomes a definite pale red as the end-point is exceeded. The exact point is largely subjective and errors in its estimation are allowed for to some extent in the standardization procedure (see Section H). However, the permanence of any supposed end-point should be checked by slowly counting to five. If the colour is not permanent a further small drop of silver nitrate solution should be added. Record the burette reading immediately to the nearest tenth of a graduated division (0.001). Note the temperature of the silver nitrate and sample (to the nearest 0.1° C) before each titration.

The following routine has been suggested as a means of attaining maximum speed in the analysis of a batch of samples when a supply of suction for the pipette and pressure for filling the burette and indicator-diluent dispenser are available. A small sink and supply of distilled water for rinsing beakers should be available to each analyst.

Whilst the bulk of the silver nitrate is running into the previous sample being titrated:

1. Fill the pipette with the sample, having noted its temperature.
2. Fill the indicator-diluent solution dispenser.
3. Rinse the beaker, which has been left draining after the second last titration.
4. Close the pipette and indicator-diluent dispenser as these become full.
5. Remove the sample bottle from under the pipette with one hand and, at the same time, dry the stem and tip of the burette by a small piece of rag or absorbent tissue held in the other hand.
6. Place the 200 ml. beaker under the pipette and under the indicator-diluent dispenser simultaneously and open the taps to allow these two solutions to enter the beaker.

Whilst the pipette is emptying and draining complete the titration of the previous sample and remove the cork from the next sample to be analysed.

7. Stop the stirrer and record the titration.
8. Remove the beaker from under the burette and invert it in the sink to drain.
9. Touch the tip of the pipette on the side of the beaker to empty it properly and then transfer this beaker, containing the sample and indicator, from beneath the pipette to beneath the burette.
10. Note the temperature of the silver nitrate solution by a thermometer placed in a small tube through which the solution flows before entering the burette.
11. Fill the burette with silver nitrate solution and start the titration.
12. Commence the cycle again at 1, above.

G. Calculations

Let V be the reading of the Knudsen burette, taken to three decimals.

Let C_b be the burette correction (positive or negative). This depends on the magnitude of the titration and is given by the manufacturers. It rarely exceeds $\pm$ 0.005.

Let C_s be the standardization correction (positive or negative) obtained as described in Section H. This correction should not exceed 0.05 - 0.1.

Let C_t be the temperature correction. This correction, which rarely exceeds a positive or negative value of 0.025, depends upon the reading V and the difference in temperature ($T_{Ag} - T_{Cl}$) between the silver nitrate solution and the sample. It is obtained from the table given at the end of this method. $T_{Ag} - T_{Cl}$ should never exceed 5° C. In making this correction it is assumed that in the range of say 14° C - 26° C the expansion of sea water and silver nitrate

solutions are small and equal to each other. If this is the case, the corrected titre so obtained is independent of temperature and is thus correct for 20° C.

Calculate the chlorosity at 20° C from the expression:

$$Cl/l_{(20)} = V + C_b + C_s + C_t$$

Evaluate the salinity from this chlorosity value from the tables of Pickard. These give the relation between Cl/l and S °/•• at various temperatures using a conversion of $Cl/l_{(t)}$ to Cl °/•• by the graphical method of Carter and Tully (J. du Conseil, 12 No. 1, 1937), and the conversion of Cl °/•• to S °/•• by the Knudsen equation. Corrections are given in this table for t = 15° C and t = 20° C from values calculated at 17.5° C. Only the t = 20° C data are used.

H. Calibration. Determination of Standardization Correction C_s. Use of Eau de Mer Normale

1. Evaluate the chlorosity of the primary standard sea water, "Eau de Mer Normale", from the equation

$$Cl/l_{20} = Cl\ °/•• \times \rho_{20} = V_a$$

where Cl °/•• is the stated chlorinity and ρ_{20} is the density of sea water of this chlorinity when at 20.0° C (NB ρ_{20} for water of a Cl °/•• value between 19.37 and 19.38 may be taken as 1.0248.) Other values are obtained from Knudsen's Hydrographic Tables.

2. Adjust the strength of the silver nitrate solution by adding small amounts of water to the solution prepared as in Section D.2, until the value of

$$V_c = V + C_b + C_t$$

obtained as described in Sections F and G, is within 0.1 or less of the chlorosity of the standard (V_a) at 20° C. Finally evaluate V_c as the mean of at least twenty determinations having a spread less than 0.025..

3. The standardization correction, C_s, for any determination will depend upon the value of $V_a - V_c$, obtained above, and the magnitude of V for the particular determination. Calculate correction intervals, υ, given by the formula:

$$\upsilon = \frac{2.V}{200\ (V_a - V_c) + 1}$$

The experimental values of V are classified according to the number of multiples of υ that they contain and the C_s values are read from a table constructed by each worker, of the form:

V	C_s
0.00 - υ	0.000
υ - 2 υ	$(V_a - V_c).\frac{\upsilon}{V_c}$
2 υ - 3 υ	$2(V_a - V_c).\frac{\upsilon}{V_c}$
3 υ - 4 υ	$3(V_a - V_c).\frac{\upsilon}{V_c}$

Values of C_s should be calculated to the nearest 0.001.

Use of Secondary Sea Water Standard

Use the silver nitrate solution, calibrated as described above, to determine the $Cl/1_{20}$ value for the secondary standard (see Section D) as the mean of ten or more duplicate determinations, a duplicate being carried out on every tenth bottle. This secondary standard should be used in preference to the Eau de Mer Normale for all routine work. The value for C_s must be determined by each worker at the commencement of each day of titrations by using a fresh bottle of secondary standard and finding the value of V_c as a mean of five determinations having a spread less than 0.025. A check of V_c should be made every 1 - 2 hours throughout the day or after every major break in the titration routine that may occur during the day. If the value of V_c, as obtained, differs by more than 0.025 from the previous mean value a new table for C_s should be constructed using the mean of a fresh set of five V_c determinations.

Temperature Correction Table

	Temperature Difference $T_{Ag} - T_{Cl}$						Temperature Difference $T_{Ag} - T_{Cl}$				
Cl/l	5	4	3	2	1	0	-1	-2	-3	-4	-5
16	0.021	0.017	0.013	0.009	0.004	0.000	0.004	0.008	0.011	0.014	0.017
16.5	.021	.017	.013	.009	.004	.000	.004	.008	.012	.015	.018
17	.022	.018	.013	.009	.004	.000	.005	.009	.013	.016	.019
17.5	.023	.018	.013	.009	.004	.000	.005	.009	.013	.016	.020
18	.024	.019	.015	.010	.005	.000	.005	.009	.013	.016	.020
18.5	.025	.019	.015	.010	.005	.000	.005	.010	.014	.017	.021
19	.026	.020	.015	.011	.005	.000	.005	.010	.015	.018	.022
19.5	.027	.021	.016	.011	.005	.000	.005	.010	.015	.019	.023
20	.028	.022	.017	.011	.006	.000	.006	.011	.016	.020	.024
	Subtract Correction					No Correction	Add Correction				

Approved June, 1957 Standard Method No. Sal. 2.A.

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Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF SALINITY BY SILVER NITRATE TITRATION

(STANDARD PRECISION METHOD)

(File N 7-1-5 June 30, 1957).

Definitions

A. Chlorinity

Halogen ions in sea water are normally estimated by argentimetry. To prevent ambiguity arising from changes in the accepted atomic weights of silver and chlorine the chlorinity, Cl °/₀₀, of sea water is defined as 0.3285234 times the weight of silver precipitated as silver halides from 1 kg. of sea water, all weighings being in vacuo.

B. Salinity

The salt content of sea water is usually expressed as salinity, S °/₀₀, a convention which approximates to the weight in grams, in vacuo, of the solids obtained from 1 kg. of sea water (weighed in vacuo) when the solids have been dried to constant weight at 480° C, the organic matter oxidized and the bromide replaced by an equivalent amount of chloride. Ocean water contains slightly more salts (halogens, carbonate and bicarbonate) than is expressed by its salinity value. In practice, the salinity is defined in terms of chlorinity by the Knudsen equation:

$$S\ ‰ = 0.030 + 1.8050\ Cl\ ‰.$$

C. Chlorosity

This value, Cl/l(t), is the quantity determined by volumetric methods

and is defined in the same manner as chlorinity except that the sample unit is 1000 ml. of sea water at a stated temperature rather than 1 kg. of sea water weighed in vacuo.

A. Capabilities of the Method

Range S °/oo 5 - 45

The following data are based on a statistical treatment of results obtained by skilled operators in a shore-base laboratory, using the procedure exactly as described.

1. Precision at the 30 °/oo Salinity Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.06}{n^{1/2}}$ °/oo.

Reject duplicate determinations if the titrations differ by more than 0.06 ml. If the duplicate titrations differ by less than this, take a mean value.

Note. The above statistical data apply at the 0.05 probability level, i.e., the odds are 19 to 1 in their favour. By this criterion two samples of sea water cannot be considered to be significantly different in salinity unless the values differ by more than 0.11 °/oo if the same standardization correction is used (see Section H below) or by more than 0.12 °/oo if different standardizations have been employed (single sample titration in both cases).

B. Outline of Method

The halogens in a 10 ml. volume of sea water are determined by titration with a silver nitrate solution using a chromate end-point, the Mohr titration. The silver solution is standardized against the same volume of sea water of known chlorosity.

C. Special Apparatus and Equipment

An automatic 10 ml. pipette and an automatic, zero adjusting, 25 ml. burette are required. An automatic dispenser of diluting solution, containing the chromate indicator, is advantageous. The titration is carried out in a 200 ml. tall-form beaker, with rapid mechanical stirring, against a white background in "yellow" artificial light from an ordinary electric light bulb.

D. Special Reagents and Solutions Required

1. Standard Sea Water

Prepare a large volume (10-20 liters) of a standard consisting of filtered sea water (preferably collected below 50 m. in the open ocean) with a chlorinity exceeding 18 °/₀₀. This sample is stabilized by adding a few crystals of thymol and is then rapidly filled into sample bottles (see Section E). Every tenth bottle is opened and analysed in duplicate, using Standard Method No. Sal. 1.A. The mean of ten or more such duplicates is taken as the chlorosity (20° C) of this standard sea water which may be used for both the present method and Standard Method No. Sal. 1.A.

2. Silver Nitrate Solution (Approximately 0.275 N).

Dissolve 48 g. of good quality silver nitrate for each liter of final solution. Use distilled water and store the solution in a dark bottle. It is desirable to make this solution in units of at least 20-40 liters when large numbers of solutions are to be analysed. This solution will require dilution

with a few per cent of water to bring it to the desired strength, as described in Section H. The solution should be well mixed in the bottle once each day or prior to each batch of titrations.

3. Indicator-Diluent Solution

Dissolve 3.5 g. of analytical quality potassium chromate, K_2CrO_4, in each liter of distilled water.

E. Sampling Procedure and Sample Storage

Use standard flat 8-ounce medicinal bottles for collecting, shipping and storage of samples used for salinity determinations. The bottles manufactured for use with size no. 6 corks should be used. The corks are soaked for 30-40 seconds in melted paraffin wax and drained and dried by placing them on a wire screen. Extruded excesses of wax are removed. The bottles are rinsed thoroughly three times with the sample and then filled to the shoulder. They are sealed by forcing the waxed corks down to a few mm. below the level of the neck. A further seal should be made within a few days by dipping the neck in melted wax. No changes in salinity will then result over a period of many years.

When these bottles, or the containers of standard water, are opened the salinity determination must be carried out within a few minutes. Repeat determinations on re-corked bottles should not be delayed for more than about one hour.

F. Experimental

Add 10 ml. of sample to a 200 ml. spoutless tall-form beaker by means of the automatic pipette and add 15 ml. of indicator-diluent solution. Titrate the solution from the 25 ml. automatic burette and switch on the mechanical stirring after about 8 ml. have entered the beaker. About one

ml. before it is judged that the end-point is reached, rinse the sides of the beaker and stirrer with a little distilled water from a wash bottle.

As the end-point approaches, the localized red precipitate formed by the silver solution will begin to spread throughout the solution. At the end-point the pale greenish-yellow colour of the contents of the beaker changes to a full yellow and then becomes a definite pale red as the end-point is exceeded. The exact point is largely subjective and errors in its estimation are allowed for to some extent in the standardization procedure (see Section H). However, the permanence of any supposed end-point should be checked by slowly counting to five. If the colour is not permanent a further small drop of silver nitrate solution should be added. Record the burette reading immediately to the nearest 0.01 of a ml. Note the average temperature of the samples T_{Cl} for each titration period of 1-2 hours (say every 20-30 samples) by a thermometer placed in a tightly packed case of bottles that has already equilibrated with the laboratory temperature. Note the average temperature of the silver nitrate solution T_{Ag} during the same period by a thermometer placed in a small tube through which the solution flows before entering the burette. If possible, T_{Ag} should be kept greater than T_{Cl} and the difference between the two should not exceed 5° C.

The following routine has been suggested as a means of attaining maximum speed in the analysis of a batch of samples when a supply of suction for the pipette and pressure for filling the burette and indicator-diluent dispenser are available. A small sink and supply of distilled water for rinsing beakers should be available to each analyst.

Whilst the bulk of the silver nitrate is running into the previous sample being titrated:

1. Fill the pipette with the sample, having noted its temperature.

2. Fill the indicator-diluent solution dispenser.
3. Rinse the beaker, which has been left draining after the second last titration.
4. Close the pipette and indicator-diluent dispenser as these become full.
5. Remove the sample bottle from under the pipette with one hand and, at the same time, dry the stem and tip of the burette by a small piece of rag or absorbent tissue held in the other hand.
6. Place the 200 ml. beaker under the pipette and under the indicator-diluent dispenser simultaneously, and open the taps to allow these two solutions to enter the beaker.

Whilst the pipette is emptying and draining, complete the titration of the previous sample and remove the cork from the next sample to be analysed.

7. Stop the stirrer and record the titration.
8. Remove the beaker from under the burette and invert it in the sink to drain.
9. Touch the tip of the pipette on the side of the beaker to empty it properly and then transfer this beaker, containing the sample and indicator, from beneath the pipette to beneath the burette.
10. Fill the burette with silver nitrate solution and start the titration.
11. Commence the cycle again at 1, above.

G. Calculations

Let V be the reading of the burette, taken to two decimals.

Let C_b be the burette correction (positive or negative). This depends on the magnitude of the titration and is given by the manufacturers or should be determined (see standard text books on analysis). It should rarely exceed $\pm$ 0.05 ml.

Let C_s be the standardization correction, obtained as described in

Section H. This correction should not exceed 0.1 ml.

Calculate the chlorosity at temperature t (see below) from the expression:

$$Cl/l_t = V + C_b + C_s$$

Evaluate the salinity from this chlorosity value from the tables of Pickard. These give the relation between Cl/l and S °/‥ at various temperatures using a conversion of $Cl/l_{(t)}$ to Cl °/‥ by the graphical method of Carter and Tully (J. du Conseil 12, No. 1, 1937), and the conversion of Cl °/‥ to S °/‥ by the Knudsen equation. Corrections are given in this table for t = 15° C and t = 20° C from values calculated at 17.5° C. Calculate:

$$t = 20 - (T_{Ag} - T_{Cl})$$

for the chlorosity temperature and enter the table at 15° C, 17.5° C or 20° C whichever is the nearest. t should rarely exceed 22.5° C which may be read as 20° C.

A temperature correction C_t may be made, as in Standard Method No. Sal. 1.A but the precision of the technique and the requirement for maximum possible speed does not merit this refinement.

H. Calibration. Determination of Standardization Correction C_s

1. Adjust the strength of the silver nitrate solution (by adding small amounts of water to the solution prepared as in Section D.2, until the value of:

$$V_c = V + C_b$$

is within 0.1 or less of the chlorosity of the standard at 20° C (expressed in ml. as V_a).

2. Evaluate V_c as the mean of five determinations, having a spread less than 0.06 ml., each day before commencing a batch of analysis.

3. The standardization correction, C_s, for any determination will depend upon the value of $V_a - V_c$, obtained above, and the magnitude of V for the

the particular determination. Calculate correction intervals, υ, given by the formula:

$$\upsilon = \frac{2.V}{200\ (V_a - V_c) + 1}$$

The experimental values of V are classified according to the number of multiples of υ that they contain and the C_s values are read from a table constructed by each worker, of the form:

V	C_s
$0.00 - \upsilon$	0.000
$\upsilon - 2\upsilon$	$(V_a - V_c) . \frac{\upsilon}{V_c}$
$2\upsilon - 3\upsilon$	$2(V_a - V_c) . \frac{\upsilon}{V_c}$
$3\upsilon - 4\upsilon$	$3(V_a - V_c) . \frac{\upsilon}{V_c}$

Values of C_s should be calculated to the nearest 0.01 ml.

Approved July, 1957 Standard Method Sal. 3.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF SALINITY BY CONDUCTIVITY MEASUREMENT

(File N 7-1-5 July 31, 1957)

Definitions cf. Addendum No. 1, page 40.

A. Chlorinity

Halogen ions in sea water are normally estimated by argentimetry. To prevent ambiguity arising from changes in the accepted atomic weights of silver and chlorine the chlorinity, Cl °/₀₀, of sea water is defined as 0.3285234 times the weight of silver precipitated as silver halides from 1 kg. of sea water, all weighings being in vacuo.

B. Salinity

The salt content of sea water is usually expressed as salinity, S °/₀₀, a convention which approximates to the weight in grams, in vacuo, of the solids obtained from 1 kg. of sea water (weighed in vacuo) when the solids have been dried to constant weight at 480° C, the organic matter oxidized and the bromide replaced by an equivalent amount of chloride. (Ocean water contains slightly more salts (halogens, carbonate and bicarbonate) than is expressed by its salinity value.) In practice, the salinity is defined in terms of chlorinity by the Knudsen equation:

$$S\ ‰ = 0.030 + 1.8050\ Cl\ ‰.$$

A. Capabilities of the Method

Range S °/₀₀ 27 - 42.5

The following data are based on a statistical treatment of results obtained by skilled operators in a shore-base laboratory, using the procedure exactly as described. Data obtained under sea-going conditions are awaited but are not expected to be very different from those given below.

1. Precision at the 35 °/₀₀ Salinity Level

The correct value lies in the range: Mean of duplicate determinations ± 0.004 °/₀₀.

Reject duplicate determinations if the readings of the salinometer differ by more than 0.14 using different cells or by more than 0.10 using the same cell. If duplicates differ by less than these amounts, take a mean value.

Note: The above statistical data apply at the 0.05 probability level, i.e., the odds are 19 to 1 in their favour. By this criterion two samples of sea water cannot be considered to be significantly different in salinity unless the values differ by more than 0.008 °/₀₀.

B. Outline of Method

The sample is placed in a conductivity cell in one arm of an AC conductivity bridge and its resistance compared with the resistance of a reference cell containing sea water which is placed in another arm of the bridge. The resistance of sea water of known salinity is then similarly compared with the resistance of the reference cell and from these values the ratio of the resistance of the unknown sample to the resistance of sea water of known salinity is obtained. Using this ratio and a calibration curve the salinity of the sample can be evaluated.

C. Special Apparatus and Equipment

The conductivity salinometer used by the Pacific Oceanographic Group is required for this method. The salinometer consists, essentially, of a high precision conductivity bridge and a constant temperature bath containing up to seven specially designed conductivity cells. The procedure for filling cells and taking a measurement with the bridge is fully described in the following method. The constant temperature bath is normally run below room temperature by means of a heating system working against refrigeration. Once adjusted the bath requires little or no attention. Directions for adjusting the bath temperature to any desired value are given in Section K. No other special equipment is required but the temperature of the laboratory in which the salinometer is used must be greater than the bath temperature employed (5° C or 15° C).

D. Special Reagents and Solutions Required

1. Standard Sea Water

The primary standard for this method must be a sample of Eau de Mer Normale with the stated Cl °/₀₀ value (near to 19.38) obtained from the Depot d'Eau Normale at Charlottenlund Slot, Charlottenlund, Denmark. To conserve this primary standard, it is essential that a large volume (20 - 40 liters) of a secondary standard be prepared, as standard sea water is required to the extent of at least 1 1/2 liters a working day. The secondary standard should, if possible, have a salinity exceeding 32 °/₀₀ and should be filtered and stabilized by adding a few small crystals of thymol. It is stored in a carboy under a layer of paraffin oil from which it may be syphoned to reach the cells in the salinometer. The salinity of the secondary standard is determined using the salinometer and Eau de Mer Normale by the procedure described in Section H.

2. Sea Water for the Reference Cell.

The salinity of the sea water used for the reference cell in the salinometer need not be known but it is desirable to use a sample of water with a salinity near to that of the samples being analysed (within 2 to 3 parts per thousand). An extra bottle of water from a cast may be set aside for this purpose or, if the salinities being measured are near to that of the secondary standard, see above, this water may also be used to fill the reference cell.

E. Sampling Procedure and Sample Storage

Use standard flat 8-ounce medicinal bottles for collecting, shipping and storage of samples used for salinity determinations. The bottles manufactured for use with size no. 6 corks should be used. The corks are soaked for 30-40 seconds in melted paraffin wax and drained and dried by placing them on a wire screen. Extruded excesses of wax are removed. The bottles are rinsed thoroughly three times with the sample and then filled to the shoulder. They are sealed by forcing the waxed corks down to a few mm. below the level of the neck. A further seal should be made within a few days by dipping the neck in melted wax. No changes in salinity will then result over a period of many years.

When these bottles, or the containers of Eau de Mer Normale, are opened the salinity determination must be carried out within a few minutes. Repeat determinations on re-corked bottles should not be delayed for more than about one hour.

F. Experimental

Procedure

1. Switch on bridge and bath and allow sufficient time for the bath to

reach temperature (Note a). Adjust the bath temperature to 15° C unless the average temperature of samples, immediately prior to measurement, is less than about 8° C when a bath temperature of 5° C should be used. The 5° C temperature is also necessary if the laboratory housing the salinometer cannot be maintained at a temperature above 15° C (see Note i). It is best to standardize on one temperature during a cruise and when once adjusted the bath requires little or no attention (Note b). The bath temperature should be checked and the value noted, by reading the thermometer every hour, as a precaution against a failure in the heating or refrigeration units going undetected for a prolonged period.

2. Zero the meter on the bridge by turning the meter gain to zero (fully counterclockwise) and adjusting the meter zeroing knob. Turn the meter gain three-quarters full up by rotating the knob in a clockwise direction. Adjust the eye by turning the gain to zero (fully counterclockwise) and adjusting the "adjust" knob until the eye opens a few degrees. Turn the gain up one-third of a turn clockwise (Note c).

3. Change the solution in the reference cell (marked R), if necessary, (Note d) with a suitable supply of sea water (see Section D.2).

4. Determine the cell constant for each cell, if necessary, (Note e) using the secondary standard sea water (see Section H).

5. Commence a sequence of measurements by rinsing and filling cell No. 1 and progressing thus to cell No. 6 in an anti-clockwise direction (Note f). Take the reading on cell No. 1 at least 15 minutes after filling this cell (Note g). Empty and rinse the cell, fill it with the next solution to be analysed and then take a reading on cell No. 2. Proceed in this fashion (Note f) round the ring of cells in an anticlockwise direction noting the time that each cell is filled and the time that the measurement is

subsequently made and checking that the time interval is never less than 15 minutes. Do all samples in duplicate, using a different cell for the repeat (Note h). Full details follow:-

Rinsing and Filling

Remove the cell stopper and fasten the tubing from the suction pump to the cell outlet. Press the pump activator until the cell is emptied. Turn off the pump and fill the cell with the solution to be analysed by using a small polyethylene funnel or by pouring the sample from a polyethylene beaker. A jigger (liquor dispensing unit) can also be used, being corked into each sample bottle in turn, but a small length of rubber tubing must be placed on the spout to give a flexible contact with the cells. Rinse the stopper and the mouth of the cell during this operation. Again empty the cell. Fill the cell with sample until it appears above the level of the lucite bath cover. Pinch the pump tubing by the finger and thumb and turn on the pump. Gently release the pressure on the tubing until the liquid in the cell is sucked down just level with the lucite bath cover (Note i). Stop the pump and replace the cell stopper. Remove the rubber tubing from the cell outlet. The above procedure, rinsing once, is adequate for most routine work. If, however, two samples, or a sample and standard sea water, are known to differ by more than about 5 °/₀₀ an extra rinsing cycle (empty and fill) should be included. This extra cycle should always be used when cell constants are determined and whenever a cell full of sea water has stood for more than about one hour, such as over a meal break (Note j).

Taking a Reading

Plug lead A into the mercury cups of the reference cell (marked R). Plug lead B into the mercury cups of the cell containing the sample to be measured (cells marked 1-6). Dial on Arm B of the bridge the value of the

cell constant for the cell concerned to two decimal places. Check that the dial marked in 0.001 ohm units is at zero. This dial is never touched. With the "eye" gain half on and the meter gain 3/4 on (see 2. above) adjust the resistances on Arm A, starting at the 100 ohm dial and moving to the left, until the best balance is obtained on the meter down to the dial marked in 0.01 ohm units. See that the dial marked in 0.001 ohm units is always reading zero. This dial is never touched. Now check that the switch is to "cap off" and turn the left hand side capacity knob until the "eye" is open as far as possible. Readjust the 0.01 ohm dial until the meter is again balanced. Check that the "eye" is fully open and, if not, tune the capacity again and once more zero the needle with the 0.01 ohm dial (Note k). If the meter does not zero exactly use the 0.01 ohm setting which gives the least meter deflection. Note the reading immediately (Note l) and write down this reading. In addition write down the cell constant showing on Arm B in a record sheet opposite the cell number, the sample number, the time of filling the cell and the time of taking the reading.

Notes

a. The bridge requires only about a minute warming period (when the "eye" should be fully lit) and should be switched off when not in use. The bath requires at least an hour to reach thermal stability at 15° C or 5° C and should be left on overnight when in continual use. For shut-down periods exceeding 24 hours, turn off the heating, stirring and refrigeration units. If a prolonged shut-down is envisaged the refrigeration coils should be emptied (see Section K).

b. For details of the procedure used to change the bath temperature see Section K.

c. The meter should be zeroed each time the bridge is switched on but is generally stable, thereafter, for many hours. The bridge is perfectly balanced when the eye is fully open. This point is most easily detected when the maximum opening is restricted by the "adjust" knob to be only a few degrees, but the exact amount is a matter of personal preference.

d. The reference cell should be closed at the exit end with a small rubber cap (policeman). If the top half of the glass stopper is greased with silicone grease (very lightly) the water in this cell need not be changed more frequently than about once a week unless the average salinity of the samples being measured is known to change markedly. It is desirable (see Section D.2.) for the salinity of the water in the reference cell to be within 2 to 3 °/₀₀ of the sample salinity.

e. The cell constants for all the cells must be determined every time that the water in the reference cell is changed. They must also be determined first thing at the commencement of each day's work and last thing before the apparatus is closed down at the end of each day's work. In addition, the constant of one of the cells, chosen at random, is determined at approximately two-hour intervals throughout the working day. If this constant changes by more than 0.1 from its previous value the cell constants for all the cells must be re-determined.

f. The circulation of the bath is such that when a cell is filled with sample solution, which may be 10° C or more different in temperature from the bath fluid, this has no effect on the temperature of the adjacent cell in an anticlockwise direction. The adjacent cell in a clockwise direction, however, is affected slightly for a period of a few minutes. When cell No. 1 is filled, therefore, it is best to wait 2 to 3 minutes before taking a reading on any other cell as the temperature of the reference cell (R) may be slightly

disturbed.

g. The main purpose of comparing the conductivity of the sea water sample with that of another sea water sample in the reference cell is that the temperature sensitivity is greatly reduced. Both water samples change their conductivity in an identical and parallel manner. However, both sample and reference cell must be at an identical temperature (to within 0.002° C or better) and to ensure this each new solution must be allowed to stand in the cell for at least 15 minutes. If the sample temperature is initially more than 10° C from the bath temperature 18 minutes should be allowed for thermal equilibrium.

h. The main purpose of a duplicate is to ensure that serious errors are not encountered due to an error in rinsing procedure or due to bubbles being trapped in the cell. For the acceptable deviation of duplicates see Section A.

i. The resistance of the electrolyte in these cells is not entirely independent of the level of the liquid in the filling arm, even when this level is many cm. above the top electrode. The level must, therefore, be reproducible from sample to sample and be the same as the level used when the cell constant was measured. The exact level is unimportant, provided that it can be reproduced to within 0.5 cm. or a little better, but experience indicates that it is not good practice to fill the cell right up to the ground glass stopper. The top of the lucite bath cover provides a useful reference level. Once the cells have come to temperature the liquid above the level of the bath should not be disturbed as it is not at bath temperature. An air-tight cell stopper ensures that ship's movement will not disturb the contents of the cell and, provided that the laboratory temperature always exceeds 15° C, there will be no convection of the warmer upper layer in the cell when the bath is at 15° C. A similar reasoning applies at a bath temperature of 5° C. Having a

refrigerated bath also minimizes the formation of nitrogen bubbles on the cell electrodes which may form if the sea water temperature is raised by more than about 10° C from its in situ temperature.

j. For reasons that are not yet fully understood, cells that have stood for several hours, or overnight, with sea water may require more rinsing than normal before they regain the highest possible reproducibility of resistance.

k. The capacity of the bridge network should be capable of being balanced by the extreme left-hand knob. The other (decade type) capacitors are used with the switch set to "Arm A" or "Arm B" but should it be necessary to employ these capacitors the cell electrodes have probably deteriorated and should be replatinized (see Section J).

l. The lead marked A may be kept permanently in cell R but the measuring lead, B, should be placed in the appropriate cell only just before a measurement is made. The current passing through the cell whilst the bridge is balanced may cause very slight heating and for this and other reasons the reading on Arm A may change slowly with time (a few units in the 0.01 ohm range). When making a measurement on solutions (or determining the cell constant, see Section H) it is best to note the first resistance balance that is obtained and not attempt to obtain a value that is strictly constant with time.

G. Calculations

Variations in the conductivity of the reference cell and variations in the behaviour of the sample cells are eliminated by frequent determinations of the cell constant (Section H) so that the readings in Arm A are always "normalized" and are directly usable for the determination of salinity. The readings of Arm A are inversely proportional to the resistance of the sample cell and hence proportional to the conductivity of the sample.

Over a relatively small range of salinity values the conductivity, expressed as the reading R or Arm A, is related to the salinity of a sample by an expression of the form:

$$S\ ^{o}/_{oo} = \alpha + \beta R + \gamma R^2 + \ldots\ldots$$

where α, β and γ are constants and higher powers of R can be neglected.

The nature of the bridge is such that residual resistances remain in Arms A and B even when the dial readings are zero. For this reason, the constant α depends on the bridge being used and cannot be assigned an absolute value. Because of the very high precision attempted in this method the constant β will also incorporate the slight relative inaccuracies of the nominal resistances in Arm A and Arm B of the bridge and will therefore depend upon the bridge being used. An empirical calibration must, therefore, be made with every bridge. The slope of the salinity/conductivity curve changes with temperature, about 0.05% per °C, and a calibration is therefore required for each bath temperature. The bath temperature must be re-set, each time it is changed, to within about $\pm$ 0.2° C of its nominal value.

For convenience a salinity of 35.000 °/$_{oo}$ has been arbitrarily assigned an R value of exactly 700.00 ohms on Arm A and, using this arbitrary fix, a careful calibration against sea water samples of known salinity has resulted in the following equations relating S °/$_{oo}$ and R at 5° C and 15° C respectively:

$$S\ ^{o}/_{oo(5^{o}C)} = 35.000 + 0.046130\ (R-700) + C$$

$$S\ ^{o}/_{oo(15^{o}C)} = 35.000 + 0.046422\ (R-700) + C$$

where C is a correction term from linearity that is the same at both 5° C and 15° C.

Salinities can be evaluated by one or the other of these equations,

according to the bath temperature, reading the small correction, C, from the parabolic graph of the function:

$$C = 4.94 \times 10^{-6} \times (R-644)^2 - 0.015.$$

For values of R between 500 and 755 (S °/‥ about 26.5 - 37.5) the salinity values may be read from the accompanying table which evaluates the relations:

$$S\ °/‥(5°C) = 4.74075 + 0.0397732.R + 4.9358 \times 10^{-6}.R^2.$$

$$S\ °/‥(15°C) = 4.53653 + 0.0400649.R + 4.9358 \times 10^{-6}.R^2.$$

These equations and tables apply as from July, 1957 but may be changed as a result of subsequent calibrations and will be issued as addenda to this method.

Note. The salinities derived from the above equations or from the accompanying tables are directly comparable with the salinities derived from chloride titration and the use of the Knudsen formula (see Standard Method No. Sal 1.A). In calibration the assumption was made that the conductivity of solutions is a function of their chlorinity when they are diluted with distilled water. The corresponding salinities were then evaluated from the Knudsen equation.

H. Calibration

1. Determination of Cell Constant

1. Fill cells 1 to 6 with secondary standard sea water rinsing twice (see Section F.5 and Notes e, g, and j).

2. Set Arm A to the correct R value for the salinity of the secondary standard at the given bath temperature. Ensure that the 0.001 ohm switch on both Arms A and B are at zero.

3. Balance Arm B in exactly the same manner as described for the balancing of Arm A in Section F.5 (see also Note 1).

4. Note the value of Arm B and take this as the cell constant applying

to all subsequent samples put in this cell until the next cell constant determination is made. If this subsequent determination shows a statistically significant change of constant it is doubtful whether the practice of correcting the sample readings between the two standardizations (by taking a "mean value" cell constant or a linearly interpolated value) has much justification unless the exact form of the cell constant variation is known. With good experimentation the constant should change very little over a period of a few hours and for work of the highest precision there is no substitute for making frequent evaluations.

2. Evaluation of the Secondary Standard Salinity

1. Undertake this determination only when the bridge and bath are working in a trouble-free manner.

2. Choose three sample cells, either at random or the three most stable cells if any behaviour differences are suspected. Rinse these cells three times and finally fill them with Eau de Mer Normale (see Section F.5).

3. Allow these cells at least 15-20 minutes to come to thermal equilibrium with the reference cell.

4. Set Arm A to the R value for the salinity of the Eau de Mer Normale which is calculated from the stated chlorinity value and the Knudsen equation (see the Definitions at the beginning of this method). The salinity must be calculated to the fourth decimal place to enable R to be calculated to the nearest 0.01 ohm.

5. Balance the bridge for each cell to determine the cell constant as described in Section G.1 above.

6. Without delay empty the cells and rinse them three times with the secondary standard and finally fill them with this standard (see Section F.5).

7. Set Arm B to the cell constant value for each cell, just evaluated, and after 15-20 minutes balance Arm A. The three values for the reading R thus obtained should have a spread not exceeding 0.15. If the spread is greater the standardization should be repeated, if not, take a mean R value of the three determinations.

8. Evaluate the salinity of the substandard from the mean R value and the equations or table (see Section G). This value is used for the carboy of secondary standard sea water and must be re-determined for each new batch of this standard.

Note. It is known that a very small number of Eau de Mer Normale ampules contain water the salinity of which is not that calculated from the stated chlorinity values. The operator must be constantly on guard against this possibility. More than one bottle of Eau de Mer Normale is required for the standardization of the secondary standard so that a "rogue" bottle should be detected by the apparently poor agreements of one cell when compared with the other two cells.

J. Care and Maintenance of the Conductivity Cells

1. General

The electrodes in the conductivity cells must never be allowed to dry or the cell be empty of water for more than a minute or two. Sea water may be left in the cells overnight or for a similar period of shut-down but for longer intervals fill the cells with distilled water (having first rinsed out salt water with one or two fillings) and close the exit end of the cells with a small rubber cap.

2. Detection of Electrode Failure

Apart from breakage or the severence of electrical contacts, both of

which are easily detectable, the only other likely defect that will develop in a cell is the deterioration of the surface of the two platinum electrodes.

If the cell constant of a particular cell changes markedly with respect to the other cells the cell is suspect. The most likely changes, however, will be found to occur in the capacity balance of the bridge which will become steadily larger as the electrodes of a cell deteriorate. Although it may still be practicable to balance the bridge network the resulting resistance is no longer of necessity a correct measure of the resistance of the sea water in the cell. The electrodes themselves contribute a resistance R_p known as the polarization resistance which is normally negligible but which increases to a significant amount as the electrodes deteriorate. Whereas the resistance of the sea water, R, should be independent of the frequency of the alternating voltage applied to a cell the R_p value depends on the frequency and may be detected by measuring the total resistance $R + R_p$, at two different frequencies. For this purpose the 400 C.P.S and 1000 C.P.S. (1 k.c.) switches are available on the bridge.

Once every week, or whenever the equipment is used after a shut-down period, or whenever a cell is suspect for any reason the cell constant should be checked using 400 C.P.S. immediately after the usual determination at 1 k.c. If the values so obtained differ by more than 0.2 ohms (the value at 400 C.P.S. will be greater) the cell requires replatinization.

3. Replatinization of Cells

The cells must be removed from the bath for replatinization.

Clean off the old platinum black coating by immersing the electrodes for a few minutes in a mixture of one part by volume of nitric acid and two parts by volume of hydrochloric acid which has been prepared a few hours before use. Rinse the cell two or three times with distilled water to remove

the cleaning fluid and then fill the cells with a solution containing 1 per cent by weight of platinic chloride, 0.03 per cent by weight of lead acetate and 2 to 3 ml. of normal hydrochloric acid per 100 ml. Place a small sheet of platinum foil about 1 cm. long and 2 to 3 mm. wide on a platinum wire down into the cell and through the hole in the back of the top electrode. With this foil in the core of each electrode (but not touching) pass a direct current of about 0.25 amp. for 1 to 2 minutes making the cell electrode the cathode. The interior of the electrodes and some of the back surface should then attain a dull grey coating. Empty the platinizing solution from the cell (retaining it for future use) and rinse once with distilled water, discarding the rinsing. Fill the cell with a 2 per cent by volume solution of sulphuric acid, insert the auxiliary electrode as described above and "clean" each electrode by passing a current of about 0.25 amp. for 1 to 2 minutes making the cell electrode the cathode. Finally rinse the cell three times with distilled water, replace it in the bath and fill with sea water. Test the cell constant again at 400 C.P.S. and 1 k.c. and check that the resistances so obtained differ by much less than 0.2 ohm (the difference should generally be undetectable.)

K. Adjusting the Bath Temperature

Full details of the construction and maintenance of the refrigeration and heating unit of the bath are not in the scope of this method. It will be necessary, however, to check and change the bath temperature from time to time and to pump refrigerant from the bath cooling coils prior to a prolonged shut-down period. Instructions for these operations are as follows:-

1. Shut-down and Start-up Operation

Note. The switch on the voltage stabilizer unit (at the back of the main panel) and the switch on the Electron-o-Therm heater control (above the main panel) should be kept permanently at "on". The main power supply can be

kept permanently alive but must have a good earthing.

For a short period shut-down (maximum 2 days, i.e., a week-end) switch off the "Pump", "Stirrer", "Heaters", "Voltage Regulator" and "Refrigerator" switches on the main panel. To start up again switch on the "Refrigerator", "Pump" and "Stirrer" switches. Then turn on the "Voltage Regulator" switch followed one minute later by the "Heaters" switch. Wait until the thermometer in the bath registers the required temperature (this may take several hours) and then allow a full hour after this for the bath to reach thermal equilibrium.

For a long period shut-down the refrigerant must be emptied from the coils in the bath and pumped into the reservoir of the refrigerator unit. To accomplish this, close the liquid line shut off of the refrigeration system by turning the yellow valve fully clockwise. Allow the system to pump until the motor stops. Turn off the oval red needle valve (fully clockwise). Open the blue and cream coloured valves when the readings should be equal and a few pounds above zero. The sight glass should be empty of refrigerant. Turn off the "Pump", "Stirrer", "Heaters", "Voltage Regulator", "Refrigerator" and "Main Power" switches. Close the blue and cream valves. To start up again switch on the "Main Power", "Refrigerator", "Pump" and "Stirrer" switches. Open the yellow valve of the refrigeration system (fully anticlockwise) and the oval red needle valve half a turn anticlockwise.

Finally adjust the bath temperature by the procedure given in the following:-

2. Bath Temperature Adjustment

General. The electrical and refrigeration system is either already turned full on or it is turned on as described in the last paragraph. Switch on the "Voltage Regulator" switch followed one minute later by the "Heaters" switch. Open the orange valve and check that the pressure is around 90-110

lbs. Close the orange valve. Open the cream valve and check that the pressure is around 40-50 lbs. Close the cream valve. Open the blue valve and keep this open during the temperature adjustment. The reading on the dial should read about 20 lbs. (always lower than the pressure on the gauge above the cream valve) when the refrigerator motor switches on and should decrease to a few lbs. above zero before the motor switches off. This valve must never read below zero or the refrigeration system will be under vacuum and oil or moist air may leak into the pipes. The two silver coloured valves on the refrigeration panel are not used. They must be kept fully closed and never touched. The pressure switch on the refrigeration panel is never touched.

To lower the bath temperature switch off the "Heaters" switch. Turn the oval red needle valve half a turn or more open and let the refrigeration take the bath temperature down to about 0.5° C lower than the desired temperature. Continue as in the next paragraph. To raise the bath temperature switch off the "Refrigerator" switch and turn up the Powerstat on the Electron-o-Therm heater control to read 85 and leave it there until the temperature is about 0.5° C lower than the desired temperature. Switch on the "Refrigerator" switch and then continue as in the next paragraph.

Adjustment. When the bath temperature is 0.5° C or a little less below the required temperature (5° C or 15° C) have the refrigerator units and heaters on, put the Powerstat to read about 50 and turn the oval red needle valve about one-eighth to one-quarter turn on (anticlockwise). Watch the thermometer carefully until the temperature is exactly correct and then immediately turn the Powerstat to zero (where it must always remain whilst the bath operates) and adjust the "Temperature Range" dial on the Electron-o-Therm until the needle of the milliammeter reads anywhere between about 20 and 90. Do not attempt any finer adjustment at this stage. If necessary use

the "Fine Temperature Adjust" to set the meter reading. It is essential that this adjustment be made when the bath temperature is exactly at the desired value as the heater control will attempt to control to the temperature of the bath when the needle is first adjusted to "float" in the 20-90 range. Now watch the meter needle. If it continually flies over to 100 the refrigeration is too strong and the oval red needle valve should be turned down. The adjustment on this valve is quite fine and the valve will probably not be needed more than an eighth or quarter turn open. Adjust this valve (do not touch the "Temperature Range" dial again) until the meter stays most of the time between 20 and 90. Now remove the screw cap from the "Thermostat Expansion Valve" unit at the bottom left of the refrigeration panel. Open the screw about half a turn a time until frost appears beneath the oval red needle valve after the refrigeration cycle has taken place once or twice. Now close the screw a quarter turn a time until this frost just disappears. Replace the screw cap on the "Thermostat Expansion Valve". Finally attempt very fine adjustments to the oval red needle valve until the milliammeter on the Electron-o-Therm heater control stays <u>most</u> of the time between 30 and 80. Turn off the blue valve. The bath is now stabilized at the desired temperature and should not require adjustment for many weeks. The refrigeration cycle (time between the motor switching off and on again) will vary with external conditions but should not be more frequent than about once every 2 to 4 minutes.

Approved December 1957

Standard Method No. Sal. 3.A

Addendum No. 1

DETERMINATION OF SALINITY BY CONDUCTIVITY MEASUREMENT

A. Capabilities of the Method

A statistical treatment of results obtained by skilled operators under sea-going conditions has shown that the precision range quoted in Standard Method No. Sal. 3.A applies unchanged to average sea-going analyses.

Rejection criteria can be relaxed somewhat and duplicate readings accepted if they agree to within 0.12 using the same cell or 0.17 using different cells (ca. S ‰ = 0.006 and 0.0085 respectively).

For shore-base work under exceptionally favourable conditions the range for the mean of duplicate determinations approaches ± 0.003 ‰. It would be unrealistic to assume that this precision can be improved significantly using the existing equipment (ref. Method Sal. 3.A).

Note. Section J. 2 and 3 should be modified as described in Standard Method No. Sal. 3.B.

Approved June, 1957 Standard Method No. O. 1.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF OXYGEN IN SEA WATER

(File N 7-1-5 June 30, 1957)

A. Capabilities of the Method

cf. Addendum No. 1, page 50.

Range 0.005 - 10 mg. atom O_2/liter.

The following data are based on a statistical treatment of results obtained under sea-going conditions by trained operators using the procedure exactly as described and standardizing the thiosulphate by a duplicate determination of the factor. If the thiosulphate factor is obtained from the mean of four or more determinations and the oxygen determination is carried out under ideal conditions the precision limits will be reduced but it cannot be assumed that the reduction will be by a factor exceeding 1.5 - 2. Exact statistical data are awaited.

1. Precision at 0.7 mg. atom O_2/l. level

The correct value lies in the range: Mean of n determinations

$\pm \frac{0.0165}{n^{1/2}}$ mg.at.O_2/l.

2. Precision at 0.03 mg. atom O_2/l. level

The correct value lies in the range: Mean of n determinations

$\pm \frac{0.003}{n^{1/2}}$ mg.at.O_2/l.

3. Limit of detection:

The smallest amount of oxygen that can be detected with certainty is about 0.005 mg.at.O_2/l.

Reject duplicate determinations if the titrations differ by:

more than 0.5 ml. in the titration range 10 - 15 ml.

more than 0.35 ml. in the titration range 5 - 10 ml.

more than 0.25 ml. in the titration range 1 - 5 ml.

more than 0.18 ml. when titrating iodate in the standardization procedure.

If the duplicate titrations differ by less than the above limits take a mean value.

Note. The above statistical data apply at the 0.05 probability level, i.e., the odds are 19 to 1 in their favour.

B. Outline of Method

A divalent manganese solution is added to the sample followed by strong alkali. The precipitated manganous hydroxide is dispersed evenly throughout the seawater sample which completely fills a stoppered glass bottle. Any dissolved oxygen is rapidly reduced and an equivalent amount of divalent manganese is oxidized to the basic hydroxides of higher valency states. When the solution is acidified in the presence of iodide the oxidized manganese again reverts to the divalent state and iodine, equivalent to the original oxygen content of the water, is liberated. This iodine is titrated with standardized thiosulphate solution. The procedure, known as the Winkler method, is a classical analytical technique.

C. Special Apparatus and Equipment

300 ml. B.O.D. (biological oxygen demand) bottles. This is all the special equipment required. The pipetting, aliquot taking and titration can be put on as "automatic" a basis as is thought desirable in any particular circumstance.

D. Special Reagents Required

1. Manganous Sulphate Reagent (Reagent No. 1)

Dissolve 480 g. of manganous sulphate tetrahydrate, $MnSO_4 \cdot 4H_2O$,

or 400 g. of manganous sulphate dihydrate, $MnSO_4 \cdot 2H_2O$,

or 365 g. of manganous sulphate monohydrate, $MnSO_4 \cdot H_2O$,

in distilled water and make the volume to 1 liter. The salt must be of analytical reagent grade to ensure the absence of ferric iron.

2. Alkaline Iodide Solution (Reagent No. 2)

Dissolve 500 g. of sodium hydroxide, NaOH, or 700 g. of potassium hydroxide, KOH, in 500 ml. of distilled water. Dissolve 150 g. of potassium iodide, KI, in 200 ml. of distilled water, mix the two solutions and dilute to 1 liter with distilled water. The potassium iodide must be of analytical reagent grade to ensure the absence of iodate. The potassium or sodium hydroxide may be of high grade commercial quality but it is safer to use analytical reagent grade.

3. 0.01 N. Standard Thiosulphate Solution

See Section H.

4. Starch Indicator Solution

Prepare a 0.1 - 0.2 per cent solution of soluble starch. A semi-preserved solution (stable for several months) may be made as follows:

Suspend 2 g. of soluble starch in 300-400 ml. of water. Add an approximately 20 per cent sodium hydroxide with vigorous stirring until the solution becomes clear (a slight permanent opalescence may remain) and allow the solution to stand for 1 - 2 hours. Add concentrated hydrochloric acid until the solution is just acid to litmus paper and then 2 ml. of glacial acetic acid. Finally dilute the solution to 1 liter with distilled water.

Discard the solution when the end-point colour is no longer a pure blue and takes on a green or brownish tint.

E. Sampling Procedure and Sample Storage

The B.O.D. bottles are rinsed twice with the sample being analysed. If the sample is obtained from a reversing bottle a length of rubber tubing should be taken from the tap to the bottom of the B.O.D. bottle and sea water introduced in such a way as to minimize turbulence and agitation of the sample. The end of the rubber tube must always be kept beneath the surface of the water as the bottle is filled. Water is allowed to overflow from the top of the B.O.D. bottle which is stoppered at once. No air should remain in the bottle. When the sample is taken from a bucket (e.g. surface samples), rinse the bottle twice and then allow the water to flow in by submerging the bottle to the mouth and gently tipping it so that the sample enters with no bubbling and the minimum of turbulence. For work of the highest accuracy the sample should be siphoned into the bottle.

Samples must be drawn into the B.O.D. bottles immediately they are taken and should be the first samples to be drawn from a reversing bottle. The sampling delay should never exceed 15 - 30 minutes. When the bottles are filled the analysis should be commenced in less than a half to one hour as oxygen may be lost when the samples warm to room temperature or by micro-biological respiration. Store the samples in the dark or in subdued light so as to minimize photosynthesis by any phytoplankton that may be present. If the analysis must be delayed "pickle" the samples by adding manganese sulphate and the alkaline iodide solutions (see Section F below). The rest of the analysis may be completed at leisure.

F. Experimental

Procedure

1. Remove the stopper from the B.O.D. bottle and add 1.0 ml. of manganous sulphate reagent (Reagent No. 1) with an automatic pipette followed at once by 1.0 ml. of alkaline iodide solution (Reagent No. 2) (note a). Restopper the bottle immediately and mix the contents thoroughly by shaking until the precipitated manganous hydroxide is evenly dispersed. No air bubbles should be trapped in the bottle.

2. When the precipitate has settled slightly (in 2 - 3 minutes) shake the bottles again. Finally allow the samples to stand until the precipitate has settled about half-way down the bottle leaving a clear supernatent solution (note b).

3. Add 1.0 ml. of concentrated (s.g. 1.84) sulphuric acid of analytical reagent quality (Reagent No. 3), restopper the bottle and mix so that all the precipitate dissolves (notes c and d). No air should be trapped in the bottle (note e).

4. Within an hour or so of acidification (note f) transfer 100 ml. of solution (200 ml. for oxygen contents less than about 0.1 mg.at.O_2/l) into a 250 ml. Erlenmeyer flask by means of a pipette or a graduated cylinder. Titrate at once with standard thiosulphate solution until a very pale straw colour remains. Add 1 - 2 ml. of starch indicator and conclude the titration, (note g).

5. Subtract any blank correction (see Section G) from the titration to obtain the corrected titration, V ml. and calculate the oxygen content of a sample from the formulae:

$$\text{mg.at.}O_2/\text{l.} = 0.0503 \times f \times V$$

When a 100 ml. aliquot is taken from a 300 ml. B.O.D. bottle,

or:

$$mg.at.O_2/l. = 0.02515 \times f \times V$$

When a 200 ml. aliquot is taken from a 300 ml. B.O.D. bottle,

or:

$$mg.at.O_2/l. = \frac{Y}{Y-2} \times \frac{5.00}{X} \times f \times V$$

When a X ml. aliquot is taken from a Y ml. bottle.

In the above expressions f is a factor, near to unity, obtained as described in Section H.

Note: The milliliters of oxygen at N.T.P. present in a liter of water can be calculated from the expression:

$$ml.\ O_2\ (N.T.P)/l. = mg.at.O_2/l. \times 11.20$$

Similarly:

$$mg.O_2/l. = mg.at.O_2/l. \times 16.00.$$

Notes

a. Place the pipette just beneath the surface of the water in the B.O.D bottle. The dense reagent solutions sink at once and as a result only water is displaced from the bottle. The outside of the alkaline iodide pipette should not get contaminated with manganese solutions as, if this occurs, the manganese is transferred to the alkaline iodide reagent bottle. Should a precipitate of higher valency manganese basic oxides appear in the alkaline iodide reagent it must be discarded.

b. The sample can be allowed to stand indefinitely at this stage provided that thermal contraction does not draw air into the bottle.

c. The top of the pipette should be placed just beneath the surface. The acid sinks and displaces about 1 ml. of solution but this contains no oxygen if the precipitate in the bottle has settled adequately.

d. If the oxygen content exceeds about 0.6 mg.at.O_2/l. a dark brown or

black precipitate may persist in the bottle after the contents have been acidified. This will dissolve if the solution is kept for a few minutes longer than usual or, if particularly stubborn, a few more drops of sulphuric acid will generally effect dissolution. A slight precipitate can be ignored provided that it is well dispersed throughout the solution before aliquots are taken (4).

e. A little carbon dioxide may be liberated when solutions are acidified but this causes no harm.

f. The acidified iodine solution is stable for many hours or days in most instances but if the water sample contains much organic matter this may be slowly oxidized by the iodine. It is advisable, therefore, not to delay the titration for longer than a few hours.

g. The titration should be taken to the end-point fairly rapidly as a return of the starch-iodine colour is sometimes experienced. Solutions should remain colourless for at least 20 seconds at the end-point.

G. Determination of Blank

The calibration procedure described in the next section is also used for the blank determination except that no iodate is added. If analytical reagent quality chemicals are used there should be no blue colour with starch. If a slight colouration results a blank correction may be ascertained by titrating with thiosulphate until the solution is colourless. If this blank correction exceeds 0.1 ml., the reagents are suspect and should be prepared afresh. The potassium iodide or manganous salt are generally the cause of the trouble. If no blue colour is formed on adding starch, check that a blue does result when 0.1 ml. or less of 0.01 N iodate is added. This guards against the presence of reductants. The blank testing should be undertaken when each new batch of reagents is prepared.

H. Calibration

1. Approximately 0.01 N. Thiosulphate Solution

Dissolve 2.5 g. of good sodium thiosulphate, $Na_2S_2O_3.5H_2O$ and 0.1 g. of sodium carbonate, Na_2CO_3, in 1 liter of water. Add 1 drop of carbon bisulphide, CS_2, per liter as a preservative. The thiosulphate solution should be prepared many liters at a time and is stable for several months. The factor (see below) will slowly decrease.

$$1.00 \text{ ml. of } 0.01 \text{ N. thiosulphate} \equiv 5.00 \times 10^{-3} \text{ mg.at.} O_2$$

2. Exactly 0.0100 N. Iodate Solution

Dry a little analytical reagent quality potassium bi-iodate, $KH(IO_3)_2$, at 105° C for one hour. Cool and weigh out 0.3250 g. Dissolve the salt in a few hundred ml. of water, warming the solution slightly if desired. Cool, transfer to a 1000 ml. measuring flask and make to the mark with distilled water. This solution is stable indefinitely.

3. Determination of the Factor f.

Fill a 300 ml. B.O.D. bottle with sea water and add 1.0 ml. of concentrated sulphuric acid (Reagent No. 3), 1.0 ml. of alkaline iodide solution (Reagent No. 2), mix, and add 1.0 ml. of manganous sulphate solution (Reagent No. 1). Withdraw approximately 100 ml. aliquots of this and similarly prepared solutions into 250 ml. Erlenmeyer flasks. Use one or two flasks for blank determinations, if necessary (see G above) and to the others add 10.00 ml. of 0.0100 N. iodate from a 10 ml. pipette. Allow the iodine liberation to proceed for at least two minutes but for not more than five minutes, during which time the solution should be at a temperature below 25° C and out of direct sunlight. Titrate the iodine with the thiosulphate solution. If v is this titre in ml. -

$$f = \frac{10.00}{v}$$

f should not vary over a period of many days or weeks and may be determined, using the mean of two titrations, at the discretion of the analyst. When a number of different workers are analysing batches of samples during a cruise it is recommended that each analyst determines f for each new batch of samples, taking the mean of two titrations. This practice helps to minimize personal errors of titration and end-point detection.

Approved June 1958 Standard Method No. O. 1.A

Addendum No. 1

DETERMINATION OF OXYGEN IN SEA WATER

Note. Reference is made to Standard Method No. O. 1.A.

A. Capabilities of the Method

For the maximum precision using Standard Method No. O. 1.A, 50 ml. aliquots in 125 ml. Erlenmeyer flasks should be used instead of the 100 or 200 ml. aliquots in 250 ml. Erlenmeyer flasks, specified in Section F. 5. Titrations should be made using a 10 ml. burette graduated in 0.05 ml. divisions and for better end-point detection the Erlenmeyer flask should be painted white on the bottom and down one side. The flask is illuminated from the side during titrations and at least 4 ml. of starch indicator are added for each determination. The precision at the 0.7 mg.at.O_2/l. level given below corresponds to the highest precision considered likely for shore-base laboratory work under near ideal conditions, with thiosulphate standardized by the mean of at least five titrations.

Precision at 0.7 mg.at.O_2/l. level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.005}{n^{1/2}}$ mg.at.O_2/l. Under routine conditions at sea the range will be greater, probably by 50 to 100 per cent. The starch end-point is comparable in precision with an electrometric end-point under sea-going conditions but the starch-iodine complex has an appreciable dissociation resulting in a slight error when starch is used. This error is not allowed for by standardization when low oxygen concentrations are being estimated (i.e. 0.1 mg.at.O_2/l. or less) and results will be up to 0.0015 mg.at.O_2/l. too low.

Approved June, 1957 Standard Method No. P. 1.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF INORGANIC PHOSPHORUS (PHOSPHATE) IN SEA WATER

(File N 7-1-5 June 30, 1957)

A. Capabilities of the Method

cf. Addendum No. 1, page 61

Range 0.08 - 5 μg.atoms P/liter

The following data are based on a statistical treatment of the results obtained under sea-going conditions by trained operators using the procedure exactly as described.

1. Precision at 3 μg.at.P./l. Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.11}{n^{1/2}}$ μg.at.P./l.

2. Precision at 0.3 μg.at.P./l. Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.055}{n^{1/2}}$ μg.at.P./l.

3. Limit of Detection

The smallest amount of phosphate that can be detected with certainty is about 0.08 μg.at.P./l.

Reject duplicate determinations if the extinction* values differ by

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* The extinction, E, is defined as $\log_{10} \frac{I_o}{I}$, where I_o and I are incident and transmitted light intensities, respectively. The Beckman DU Spectrophotometer is calibrated directly in extinction units. If the absorptiometer employed reads per cent transmission, T, calculate E as $\log_{10} \left(\frac{100}{T}\right)$.

more than 0.05 in the extinction range 0.5 - 1.0

or more than 0.025 in the extinction range 0.1 - 0.5

or more than 0.02 in the extinction range 0.03 - 0.1.

If the duplicate extinction values differ by less than the above limits, take a mean value.

Note. The above statistical data apply at the 0.05 probability level, i.e. the odds are 19 to 1 in their favour.

B. Outline of Method

The seawater sample is allowed to react with molybdate under acidity conditions which permit the formation of phosphomolybdate without the formation of silicomolybdate from any silicic acid present. The phosphomolybdate complex is then reduced by stannous chloride to give the blue reduced complex and the extinction of the resulting solution is measured using 10 cm. cells and light of wavelength near to 7000 A.

C. Special Apparatus and Equipment

A Beckman DU Spectrophotometer or any other seaworthy spectrophotometer capable of measuring the extinction of light of wavelength near to 7000 A.

Spectrophotometer or absorptiometer cells having a path length of at least 10 cm. and holding less than 90 ml. of solution.

130 ml. capacity polyethylene bottles, with screw caps, marked on the side at 100 ml.

D. Special Reagents Required

1. Molybdate Reagent (Reagent No. 1)

Prepare 50 per cent V/V sulphuric acid by pouring 300 ml. of concentrated (s.g. 1.82) analytical reagent quality sulphuric acid into 300 ml. of

distilled water. Cool to room temperature and make the volume to 600 ml. with a little extra water. Dissolve 20 g. of analytical reagent quality ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (preferably finely crystalline) in 200 ml. of distilled water. Add this solution to the 600 ml. of 50 per cent V/V sulphuric acid, stirring vigorously. The resulting solution is stable for many months if stored in a dark bottle with a plastic or glass stopper.

2. Stannous Chloride Stock Solution

Dissolve 4.3 g. of analytical reagent quality stannous chloride dihydrate, $SnCl_2.2H_2O$, in 40 ml. of concentrated (s.g. 1.18) hydrochloric acid. Warm a little, if necessary, to assist solution. Pour 160 ml. of boiled-out distilled water in a polyethylene bottle whilst the water is still near the boiling point. Add the hydrochloric acid solution of stannous chloride and a small piece of granular tin metal and cover the solution with a thin layer of mineral oil. The solution, under oil, is stable for many months.

3. Stannous Chloride Working Solution (Reagent No. 2)

Dilute 10 ml. of the above stock solution to 50 ml. using a 5 per cent V/V hydrochloric acid solution in boiled-out water. This solution may be kept for several days under mineral oil but is best made up for each batch of determinations. If not stored under oil, the solution should be made fresh every day.

E. Sampling Procedure and Sample Storage

130 ml. polyethylene bottles should be filled completely with sample after rinsing them twice with the water to be analysed. The analysis should be commenced as soon as possible, preferably within half an hour, certainly within 1 - 2 hours. Samples should be kept in the dark and not warmed to room temperature until the analysis is to be commenced. If the analysis has

has to be delayed for more than 1 - 2 hours refrigerate the samples to 0° C or less. If the samples are stored at 0° C or less with one drop of chloroform in each bottle, they should be stable for at least a month. Quick freezing in a 40 per cent glycol bath at -20°C (freeze to this temperature within 30 minutes of collection) stabilizes samples for many months and this technique should be used for the most precise work, on samples drawn from the euphotic or regeneration zones.

F. Experimental

Procedure

1. Warm the samples to a temperature between 18° C and 23° C in a thermostated water bath or by placing the bottles in warm water to bring them within this temperature range and then storing them in a laboratory which has a uniform temperature between 18° C and 23° C (note a).

2. Measure the extinction of samples to obtain the turbidity correction (note b; see also 4, below, for the necessary precision of measurements).

3. Add 1.0 ml. of molybdate solution (Reagent No. 1) from an automatic pipette to 100 ml. of sample and mix the solution (note c). Allow the sample to stand for 3 minutes (note d). Add 0.5 ml. of dilute stannous chloride (Reagent No. 2) swirling the sample to ensure rapid mixing (note e).

4. Exactly 10 minutes after adding the stannous chloride, measure the extinction of the solution in a 10 cm. cell against distilled water (note f). A wavelength of 7000 A and slit width of 0.03 mm. should be used with the Beckman DU Spectrophotometer (red sensitive photocell). If a filter-type absorptiometer is used choose a filter having a maximum transmission in the region of 7000 A (note g). Record extinction values (and corrected values, see 5 below) to the nearest 0.001 unit in the range 0.000 - 0.200, to the nearest 0.0025 unit in the range 0.200 - 0.400 and to the nearest 0.005 for

extinction values exceeding 0.400. Unless adjacent samples are known to have extinction values within about 25 per cent of each other the absorptiometer cell should be rinsed with each new solution before filling.

5. Correct the measured extinction by subtracting both the turbidity and reagent blanks (see Section G). Calculate the phosphate concentration in microgram atoms of phosphate phosphorus per liter (μg.at.P./l) from the expression:

$$\mu g.at.P./l = \text{corrected extinction} \times F$$

where F is the factor for each batch of samples obtained as described in Section H below. Report results to three significant figures. Silicon, present in the amounts normally reported for sea water, causes no interference. Arsenic will interfere if present in the pentavalent form and will be recorded as phosphorus. The interference is normally negligible (less than 5 per cent of the phosphorus) but for the most precise work if the concentration of As^V is known, say Z μg.at.As^V/l., the phosphorus result may be corrected by subtracting 0.4 x Z.

Notes

a. The extinction obtained from a given amount of phosphorus depends on the temperature, increasing about 1 per cent for each increase in temperature of 1° C. To allow for this, the temperature of samples and standards (see Section 4) should be within 1 - 2° C of each other.

b. This measurement is rarely required for every sample (see Section G). If the turbidity gives an extinction exceeding about 0.05 the suspended matter may adversely affect the method and solutions should be filtered.

c. The extinction for a given amount of phosphorus depends upon the concentration of moloybdate which should not vary within each batch of samples and standards. The exact volume of sample is not critical but should lie between 95 and 105 ml.

d. Results are markedly more reproducible if the molybdate and phosphate react for a few minutes before adding reductant. Prolonged standing at this stage should be avoided as organically combined phosphorus and any particulate inorganic phosphate will slowly degrade to phosphoric acid.

e. The extinction from a given amount of phosphorus depends upon the concentration of stannous chloride. A decrease of 10 per cent from the recommended concentration decreases the extinction by rather more than 1 per cent. Unprotected dilute stannous chloride solutions oxidize by this amount within an hour or two but the effect is allowed for by the device of calibrating with each batch of determinations. The 0.5 ml. of reductant need not be exact provided that it is the same for samples and standards. The dependence of extinction on salinity is discussed in Section H, below.

f. The extinction of the blue reduced phosphomolybdate complex is not constant with time. It rises to a maximum, stays constant and then decreases. The time range for this maximum varies with temperature approximately as follows:

Temperature	Time Range
11° C	14 - 23 minutes
14° C	12 - 18 minutes
16° C	11 - 15 minutes
23° C	5 - 14 minutes

If solutions are at a temperature between 18° C and 23° C a waiting period of 10 minutes will ensure maximum colour formation. In routine analysis it is simplest to adhere rigorously to the 3-minute and 10-minute periods stated in 3 and 4. This time variability is a weakness in the use of stannous chloride but the reagent gives the greatest sensitivity of any known reductant.

g. The absorption maximum for the reduced phosphomolybdate complex covers a broad wavelength and the exact value is not critical between say 6800 A and 8000 A. 7000 A is about the optimum.

G. Determination of Blanks

1. Cell to Cell Blanks

When both sample and distilled water cells are filled with distilled water the extinction of one against the other should be 0.000. Due to slight optical defects a slight positive or negative value may be found. This is allowed for when turbidity blanks are subtracted (see below) but the value should be found when determining the reagent blank. The water in the distilled water cell should be changed every day as marked turbidities can result even in distilled water if it remains in the cell for too long.

2. Reagent Blanks

Carry out the method exactly as described in Section F, paragraphs 2-4 inclusive, using distilled water in place of 100 ml. of sea water. Correct the resulting extinction for the cell to cell blank. The reagent blank should not exceed 0.02. If this occurs use redistilled water. Should the blank persist the ammonium molybdate reagent is suspect. The reagent blank, although small, is not insignificant for the most accurate work or when less than 1.5 μg.at.P./l is being determined. It should be measured for each new batch of molybdate reagent and checked at weekly intervals during a cruise.

3. Sea Water Turbidity Blanks

These may be a very appreciable fraction of the total extinction in surface waters and should be determined on the surface and 10 m. samples of each cast. Measure at progressively greater depths until the value becomes approximately constant. This value (generally less than at 0.01 below 25 m. in offshore waters) is then roughly equal to the cell to cell blank (G.1. above) and may often be slightly negative.

Turbidity blanks should be measured on the sample solutions after they

have been warmed to room temperature, just prior to adding the molybdate reagent. If 130 ml. polyethylene bottles are filled to the brim with sample, enough is present for the turbidity blank leaving nearly 100 ml. for analysis. A few ml. may be poured back from the absorptiometer cell if necessary.

H. Calibration

1. Standard Phosphate Solution

Dissolve 0.340 g. of anhydrous potassium dihydrogen phosphate, KH_2PO_4, in 1000 ml. of distilled water. Store in a dark bottle with 1 ml. of chloroform. The solution is stable for many months.

1 ml. $\equiv$ 2.5 μg.at.P.

Dilute 10.0 ml. of this solution to 1000 ml. with synthetic sea water (see below). Store in a dark bottle with 1 ml. of chloroform. The solution should be stable for many weeks but, for safety, should be made afresh about once every 10 days.

1 ml. $\equiv$ 2.5 x 10^{-2} μg.at.P.

1 ml. $\equiv$ 0.25 μg.at.P./l in 100 ml. of sea water sample.

2. Synthetic Sea Water

Dissolve 25 g. of analytical reagent quality sodium chloride, NaCl, and 8 g. of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, in each liter of distilled water. This solution is best made up in 5 - 20 liter quantities at a time and stored in polyethylene. The phosphorus blank extinction on this solution should not exceed 0.2 - 0.25 initially. On storing the solution, a decrease in blank is normally observed due to the abstraction of inorganic phosphate by living organisms. This is advantageous and it is recommended that the synthetic sea water be prepared several weeks before its anticipated use, when a blank as low as 0.05 - 0.1 should result. If bacterial growth becomes

excessive, a turbidity may result, but this will form mainly at the bottom of large storage vessels and will not give trouble unless the bottom layer is disturbed. If the extinction is satisfactory (i.e., less than 0.15) the solution may be filtered and further bacterial action inhibited by the addition of a few crystals of thymol.

3. Procedure

With every batch of samples prepare three standard solutions consisting of 12.0 ml. of the dilute phosphate solution (equivalent to 3.0 μg.at.P./l) made to a volume of exactly 100 ml. with synthetic sea water in a graduated measuring cylinder. Transfer the solutions to three dry polyethylene bottles and fill two more bottles with synthetic sea water (95 - 105 ml.) to act as blanks. Carry out the phosphate determination as described in Section F above (paragraphs 2-4). The standards and synthetic sea water blanks should be placed in the middle of every batch of samples and treated exactly as the other samples.

Calculate the factor F from the expression:

$$F = \frac{3.00}{E_s - E_b}$$

where E_s is the mean extinction of the three standards and E_b is the mean extinction of the two blanks (not corrected for cell to cell blanks). The value for F should be between about 4 and 4.5.

Note. The factor F depends on various conditions, described in the notes of Section F, and compensates for changes in these conditions from batch to batch of samples. In addition, F is a function of the salinity of the seawater samples. With salinities of 20 °/₀₀ and greater the factor determined with the synthetic sea water, above, may be used. With salinities between 10 °/₀₀

and 20 °/₀₀ the factor will be up to 5 per cent too high and if samples are known to be in this range of salinity the factor should be determined on a synthetic sea water prepared by diluting the above solution with an equal volume of distilled water. If the salinity is less than 10 °/₀₀ F changes rapidly and should be determined using a solution within a few parts per thousand of the salinity of the samples concerned. The factor obtained with fresh water is some 18 per cent less than that pertaining to water of a salinity exceeding 25 °/₀₀.

Approved December 1957 — Standard Method No. P. 1.A

Addendum No. 1

DETERMINATION OF INORGANIC PHOSPHORUS (PHOSPHATE) PRESENT IN SEA WATER IN AMOUNTS LESS THAN 0.5 MICROGRAM ATOMS PER LITER

Note. Reference is made to Standard Method No. P. 1.A.

A. Capabilities of the Method

The following method is essentially the same as Standard Method No. P. 1.A except that a different technique is used for the extinction measurements. The technique is designed to minimize the errors that may occur in the estimation of amounts of phosphorus less than about 0.5 μg. atoms P/l that are present in turbid samples. In general it should only be necessary to employ this modification for phosphorus depleted surface waters near to a land drainage area. (In no case should a phosphorus determination be attempted, without filtration of the sample, if the turbidity blank exceeds about 0.1 on a 10 cm. cell.)

Precision at the 0.3 μg.at.P/l level has not been evaluated as conditions can be so variable. The precision should be comparable and generally much higher than that quoted in Standard Method No. P. 1.A instead of much worse, as would be the case were the analysis of low phosphorus high turbidity waters attempted without using the present modification.

The method described in this addendum could be used to determine phosphorus in all samples but the additional complexity of manipulation is not justified except in the circumstances outlined above.

B. Outline of the Method

The seawater sample is allowed to react with molybdate under acidity conditions that permit the formation of phosphomolybdate without the formation of silicomolybdate from any silicic acid present. The extinction of this solution is measured in a 10 cm. cell using light of wavelength near to 7000 A. Stannous chloride is then added to produce a blue reduced complex and the extinction is re-measured. The difference between the second and first extinction value is a measure of the phosphate present in the sample.

C. Special Apparatus and Equipment

See Standard Method No. P. 1.A.

D. Special Reagents Required

See Standard Method No. P. 1.A.

E. Sampling Procedure and Sample Storage

See Standard Method No. P. 1.A. Samples should be vigorously shaken just before the analysis is commenced.

F. Experimental

Procedure

1. Warm the samples to a temperature between 18° C and 23° C in a thermostated water bath or by placing the bottles in warm water to bring them within this temperature range and then storing them in a laboratory which has a uniform temperature between 18° C and 23° C (note a).

2. Add 1.0 ml. of molybdate solution (Reagent No. 1) from an automatic pipette to 100 ml. of sample and mix the solution (note c). Transfer the

solution to a 10 cm. cell that has previously been rinsed several times with distilled water and drained. A little water left behind in the cell before the sample is added does no harm (it should not exceed 1 to 2 ml.) and the cell should not be rinsed with sample. Three minutes after adding the molybdate to the sample (note d) measure the extinction with a Beckman DU Spectrophotometer, at a wavelength of 7000 A and slit width of 0.03 mm. using the red sensitive photocell. If a filter-type absorptiometer is used choose a filter having a maximum transmission in the region of 7000 A (note g). Record extinction values to the nearest 0.001 unit. Let this extinction be E_m.

3. Pour the solution from the cell back into the vessel containing the remainder of the sample and molybdate. Drain the cell but do not wash it. Add 0.5 ml. of dilute stannous chloride (Reagent No. 2) swirling the sample to ensure rapid mixing (note e). Refill the 10 cm. cell with the reduced sample solution, rinsing the cell once, and exactly 10 minutes after adding the stannous chloride re-measure the extinction on the spectrophotometer or absorptiometer (note f). Let this extinction be E_r. Evaluate $(E_r - E_m)_{sample}$.

Notes

See the notes to Section F of Standard Method No. P. 1.A.

G. Determination of Blanks

Only a reagent blank is necessary with this method as "cell to cell" and "turbidity" blanks are eliminated by the nature of the procedure. The reagent, however, may constitute an appreciable fraction of the total extinction due to phosphorus in the sample and should be determined each

time samples are analysed. Carry out the method exactly as described in Section F above using distilled water in place of the 100 ml. of seawater sample. Evaluate $(E_r - E_m)_{distilled}$.

H. Calibration

This is carried out exactly as described in Standard Method No. P. 1.A and samples may conveniently be analysed by the procedure described in this addendum at the same time as a batch of analyses is undertaken by the main method. The same factor, F, is used for both methods.

I. Calculations

$$\mu g.at.P/l = \left[(E_r - E_m)_{sample} - (E_r - E_m)_{distilled} \right] \times F.$$

Approved July, 1957 Standard Method No. P. 2.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF TOTAL PHOSPHORUS IN SEA WATER

(AND ORGANIC PHOSPHORUS BY DIFFERENCE)

(File N 7-1-5 July 31, 1957)

A. Capabilities of the Method

cf. Addendum No. 1, page 79.

This method cannot be used for fresh or brackish water. It is designed for sea water, free from excessive sewage effluent, of salinity between 15 °/oo and 36 °/oo.

Range 0.08 - 5 μg. atoms P./liter.

1. Precision at 2.5 μg.at.P./l. Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.13}{n^{1/2}}$ μg.at.P./l.

2. Precision at 0.5 μg.at.P./l. Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.08}{n^{1/2}}$ μg.at.P./l.

3. Limit of Detection

The smallest amount of phosphorus that can be detected with certainty is about 0.08 μg.at.P./l.

Reject duplicate determinations if the extinction* values differ by

* The extinction, E, is defined as $\log_{10} \frac{I_o}{I}$, where I_o and I are incident and transmitted light intensities, respectively. The Beckman DU Spectrophotometer is calibrated directly in extinction units. If the absorptiometer employed reads per cent transmission, T, calculate E as $\log_{10}\left(\frac{100}{T}\right)$.

more than 0.05 in the extinction range 0.5 - 1.0

or more than 0.025 in the extinction range 0.1 - 0.5

or more than 0.02 in the extinction range 0.03 - 0.1.

If the duplicate extinction values differ by less than the above limits, take a mean value.

Note. The above statistical data apply at the 0.05 probability level, i.e., the odds are 19 to 1 in their favour.

4. Precision of Organic Phosphorus Determination

The present method determines the phosphorus present as inorganic phosphate, as dissolved organically combined phosphorus and as phosphorus present in suspended particulate matter. The latter is present largely as organic detritus but some insoluble inorganic phosphorus may occur in turbid inshore waters. The amount of insoluble phosphorus will rarely exceed a few tenths of a microgram atom of phosphorus per liter. If required separately it should be determined directly in the solid matter retained when a sea water sample is filtered through a millipore filter.

If the determination of inorganic phosphate is carried out by Standard Method No. P. 1.A. immediately a sample is taken from the sea, then the difference between the total phosphorus result and this inorganic phosphate result is largely a measure of the organic phosphorus that was present in the sea water when it was sampled. As this value is obtained as the relatively small difference of two relatively large numbers the precision is never great unless many replicate determinations are made of both inorganic and total phosphorus. The variance can be calculated by normal statistical practice knowing the statistical data quoted above and in Section A of Standard Method No. P. 1.A. For example, if the inorganic and total phosphorus are both in the range 2 -

2.5 μg.at.P./l. the correct value of the organic phosphorus will lie in the range: Mean of n determinations $\pm \frac{0.16}{n}$ μg.at. organic P./l. when both inorganic and total phosphorus have been separately determined as the mean of n determinations and their means then subtracted. Similarly the limit of detection of organic phosphorus when the total phosphorus is around 2 μg.at.P./l, approximates to $\pm \frac{0.15}{n^{1/2}}$ μg.at. organic P./l. As the level of soluble organic phosphorus will rarely exceed 0.8 μg.at. organic P./l, the mean of at least five determinations should be made for the uncertainty to be below 10 per cent of the quantity being determined. It is important, therefore, that this number of determinations be made of the inorganic phosphorus, when the samples are taken on a cruise, as well as of the total phosphorus which is carried out later in a shore laboratory.

B. Outline of Method

A 50 ml. sample of sea water is evaporated with perchloric acid. Chloride is replaced by perchlorate and much of the arsenic is volatilized. The residue is heated and any organic matter is oxidized liberating phosphorus as inorganic phosphate. The total phosphate is then determined, after adding 50 ml. of water, by a modification of Standard Method No. P. 1.A.

C. Special Apparatus and Equipment

A Beckman DU spectrophotometer or any other absorptiometer capable of measuring the extinction of light of wavelength near to 7000 A.

Spectrophotometer or absorptiometer cells having a path length of at least 10 cm. and holding less than 40 ml. of solution.

One hundred and twenty-five ml. pyrex Erlenmeyer flasks. Three small dents, 1 to 2 mm. deep are made in the lip of each flask symmetrically placed round the rim. The flasks are covered with 2-inch diameter coverglasses.

7 cm. ± 0.5 cm. lengths of melting-point capillary closed at one end, one for each flask.

Full details for the preliminary cleaning and conditioning of this glass are given in Section G below.

D. Special Reagents Required

1. Perchloric Acid Solution (Reagent No. 1)

Dilute 300 ml. of 70-72 per cent analytical reagent quality perchloric acid to 1 liter with distilled water. Store in a clean pyrex glass bottle.

2. Potassium Iodide Solution (Reagent No. 2)

Dissolve 5 g. of analytical quality potassium iodide in 100 ml. of water. Store in a glass stoppered dropping bottle. The solution is stable and need not be discarded when a slight brown coloration develops.

3. Dilute Ammonia Solution (Reagent No. 3)

The ammonia solution must be taken from a freshly opened bottle of concentrated ammonia (s.g. 0.9) solution of analytical reagent quality. Dilute 100 ml. of this solution to 500 ml. with distilled water and store in a tightly stoppered polyethylene bottle. The solution is stable except for a slight loss of ammonia gas which may become appreciable as the solution is used. For safety it should be prepared fresh every week if in continual use or, in any event, every 2 to 3 weeks.

4. Dilution Water (Reagent No. 4)

This is distilled water to which has been added 2.0 ml. of concentrated hydrochloric acid (s.g. 1.14) for every liter. The water should be stored in a polyethylene bottle or carboy.

5. Molybdate Reagent (Reagent No. 5)

Prepare 50 per cent V/V sulphuric acid by pouring 300 ml. of concentrated (s.g. 1.82) analytical reagent quality sulphuric acid into 300 ml. of distilled water. Cool to room temperature and make the volume to 600 ml. with a little extra water. Dissolve 20 g. of analytical reagent quality ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (preferably finely crystalline) in 200 ml. of distilled water. Add this solution to the 600 ml. of 50 per cent V/V sulphuric acid, stirring vigorously. The resulting solution is stable for many months if stored in a dark bottle with a plastic or glass stopper.

6. Sodium Sulphite Solution (Reagent No. 6)

Dissolve 3 g. of analytical reagent quality anhydrous sodium sulphite, Na_2SO_3, in 100 ml. of distilled water. Store in a small tightly-stoppered polyethylene bottle. Prepare fresh once a month. Transfer a little of this solution for use into a dropping bottle but discard any remaining solution after a batch of analyses is complete.

7. Stannous Chloride Reagent Stock Solution

Dissolve 4.3 g. of analytical reagent quality stannous chloride dihydrate, $SnCl_2.2H_2O$, in 40 ml. of concentrated (s.g. 1.18) hydrochloric acid. Warm a little, if necessary, to assist solution. Pour 160 ml. of boiled-out distilled water in a polyethylene bottle whilst the water is still near the boiling point. Add the hydrochloric acid solution of stannous chloride and a small piece of granular tin metal and cover the solution with a thin layer of mineral oil. The solution, under oil, is stable for many months.

8. Stannous Chloride Working Solution (Reagent No. 7)

Dilute 10 ml. of the above stock solution to 100 ml. using a 5 per cent V/V hydrochloric acid solution in boiled-out water. This solution must be

made up fresh for each batch of determinations and should not be stored for longer than 2 to 3 hours.

E. Sampling Procedure and Sample Storage

Note. If an accurate estimation of organic phosphorus is required the sample for inorganic phosphorus must be analysed without delay.

The sample for total phosphate must be taken within about 1 to 2 hours of surfacing sampling bottles or taking a surface sample. As it will rarely be possible to carry out the present method on board ship, it will be necessary to store samples. Small pyrex bottles or boiling tubes may be used, but never soft glass, and exactly 50 ml. of sample should be pipetted into the storage vessel which has previously been cleaned by evaporating and fuming about 10 ml. of Reagent No. 1 in each container for an hour, subsequently rinsing with distilled water. The bottle or test tube should be tightly corked but subsequent evaporation of the sample or changes in the form of the phosphorus present causes no errors. The deposition of phosphorus containing material on the walls of the storage vessel, however, necessitates the cleaning of the inner surface before analysis commences (see Section F below).

F. Experimental

Procedure

1. The quantity of perchloric acid solution used in this method depends upon the approximate salinity of a sample (Note a). The reagent volume should be correct to the nearest 0.5 ml. according to the following:

S °/oo	Volume of Reagent No. 1
15	5.5
20	6.5
25	7.5

S °/oo	Volume of Reagent No. 1
30	8.5
33	9.5
36	10.0

Pour the contents of the sample bottle (containing 50 ml. initially) into the special 125 ml. Erlenmeyer flask. Add the requisite volume of Reagent No. 1 to a suitable dispensing device and introduce about half of the reagent to the sample vessel. Rub the sides of the vessel vigorously with this reagent by means of a small rubber policeman and pour the acid into the flask (Note b). Repeat this operation with the remainder of Reagent No. 1 and finally rinse the bottle and policeman into the flask with a little distilled water (not more than about 10 ml.).

2. Place a capillary into the flask, open end downwards, (Note c) and evaporate the contents of the flask with vigorous boiling on a hot plate until the volume is reduced to about 15-20 ml. Reduce the heat somewhat, add 2 to 3 drops (ca. 0.1 ml.) of potassium iodide solution (Reagent No. 2) and place the coverglass over the mouth of the flask (Note d).

3. Continue the evaporation at a rapid rate until solid <u>just</u> begins to separate. Lower the temperature a little and continue the evaporation more cautiously until all water and acid is removed and perchloric acid refluxes down the sides of the flask (Note e). Finally place the flasks on the hottest part of a hot plate, ca. 400° C, and heat for 10 minutes with the perchloric refluxing. Only a very slight loss of vapour should occur if a coverglass is in place.

4. Remove the flask and allow it to cool until it can be held against the palm of the hand. Add 5 ml. of dilute ammonia solution (Reagent No. 3) and rinse the coverglass into the flask with a few drops of distilled water. Place

the flask back on a moderate hot plate and boil rapidly to remove all excess ammonia. Then evaporate the contents to dryness by boiling gently. If the boiling is very rapid at the time solid commences to separate very bad "bumping" may occur. As the contents become solid remove the coverglass and continue the evaporation until all the water is removed but do not overheat (Note f).

5. Remove the flask from the hot plate and allow it to cool to room temperature. Add, by means of a pipette, exactly 50 ml. of dilution water (Reagent No. 4) and warm the solution slightly until a clear solution is obtained (Note g). Finally cool the sample to a temperature between 18° C and 23° C in a water bath (Note h).

6. Add 0.5 ml. of molybdate solution (Reagent No. 5) from an automatic pipette (Note i). Add at once 2 to 3 drops (0.1 ml.) of sodium sulphite solution (Reagent No.6) (Note j). Allow the sample to stand for 3 minutes (Note k). Add 0.5 ml. of dilute stannous chloride (Reagent No. 7) from an automatic pipette, swirling the sample to ensure rapid mixing (Note l).

7. Exactly 6 minutes after adding the stannous chloride, measure the extinction of the solution in a 10 cm. cell against distilled water (Note m). A wavelength of 7000 A and slit width of 0.03 mm. should be used with the Beckman DU Spectrophotometer (red sensitive photocell). If a filter-type absorptiometer is used choose a filter having a maximum transmission in the region of 7000 A (Note n). Record extinction values (and corrected values, see 8 below) to the nearest 0.001 unit in the range 0.000 - 0.200, to the nearest 0.0025 unit in the range 0.200 - 0.400 and to the nearest 0.005 for extinction values exceeding 0.400. Unless adjacent samples are known to have extinction values within about 25 per cent of each other the absorptiometer cell should be rinsed with each new solution before filling.

8. Correct the measured extinction by subtracting a reagent blank (see Section G). Calculate the total phosphate concentration in microgram atoms

of total phosphorus per liter (μg.at.P./l.) from the expression:

$$\mu\text{g.at.P./l.} = \text{corrected extinction} \times F$$

where F is the factor for each batch of samples evaporated (determined as described in Section H below.) Report results to three significant figures.

Notes

a. For correct neutralization, see 4, and to ensure satisfactory behaviour at the fuming stage, see 3, the excess perchloric acid, after the chloride in the sea water is displaced, should lie in the range of about 0.4 - 0.8 ml. of 70 per cent acid. The quantities given in Section F.1. ensure this, if judged to the nearest 0.5 ml. The salinity need only be known to about 1 °/₀₀.

b. If bacterial or algal growth have occurred since the sample was taken some phosphorus may be abstracted from the solution and held on the walls of the vessel in organic combination.

c. Severe "bumping" is encountered in the early stages of evaporation unless an antibumping device is added, such as the capillaries specified in Section C.

d. Any arsenic present in the seawater sample is reduced to the trivalent form by iodide in acid solutions and is subsequently lost be evaporation as chloride. Tests have shown that arsenic initially present to the extent of several microgram atoms of As $\overline{V}$ per liter gives no interference.

e. It is essential that all hydrochloric acid vapour and water is removed at this stage. Some spurting of the semi-solid mass in the flask will occur as the water is finally removed but this will not be excessive and may be disregarded as the sides of the flask will be cleaned during the subsequent refluxing of perchloric acid. The refluxing of perchloric acid is quite characteristic and is seen as a heavy oily ring of liquid pouring down the sides. The top of the flask and the coverglass will become almost dry and only a little

heavy vapour will escape from the mouth of the flask. The fumes in the flask almost disappear unless a little air is blown in, when a dense white vapour forms.

f. This treatment with ammonia and evaporation ensures that a neutral dry residue of reproducible volume is left irrespective of the amount of excess perchloric acid left at the fuming stage (3). Subsequent neutralization with varying volumes of alkali is thus avoided making for a more rapid and reproducible technique with easier blank control. The contents of the flask should not be overheated at this stage. A few tenths of a ml. of water held on the sides of the flask may be disregarded as this will largely evaporate when the flask is allowed to cool.

g. The residue, after ammonia treatment and evaporation, contains a little magnesium hydroxide. The small amount of hydrochloric acid present in the dilution water ensures that all hydroxides dissolve but the excess acid is then too small to interfere with subsequent colour development.

h. The extinction obtained from a given amount of phosphorus depends on the temperature, increasing about 1 per cent for each increase in temperature of 1° C. To allow for this, the temperature of samples and standards (see Section H) should be within 1 - 2° C of each other.

i. The extinction for a given amount of phosphorus depends upon the concentration of molybdate which should not vary within each batch of samples and standards.

j. During the strong heating with perchloric acid traces of chlorine or chlorite may form. If these compounds persist to the colour development stage of the method very serious errors may be introduced. The small addition of sulphite causes no interference to the colour development but ensures the absence of any traces of oxidants that may arise from the perchloric acid.

k. Results are markedly more reproducible if the molybdate and phosphate react for a few minutes before adding reductant.

l. The extinction from a given amount of phosphorus depends upon the concentration of stannous chloride. A decrease of 10 per cent from the recommended concentration decreases the extinction by rather more than 1 per cent. Unprotected dilute stannous chloride solutions oxidize by this amount within an hour or two but the effect is allowed for by the device of calibrating with each batch of determinations. The 0.5 ml. of reductant need not be exact provided that it is the same for samples and standards.

m. The extinction of the blue reduced phosphomolybdate complex is not constant with time. It rises to a maximum, stays constant and then decreases. If solutions are at a temperature between 18° C and 23° C a waiting period of 6 minutes will ensure maximum colour formation (not 10 minutes as in Standard Method No. P. 1.A.) In routine analysis it is essential to adhere rigorously to the 3-minute and 6-minute periods stated in 6 and 7. This time variability is a weakness in the use of stannous chloride but the reagent gives the greatest sensitivity of any known reductant.

n. The absorption maximum for the reduced phosphomolybdate complex covers a broad wavelength and the exact value is not critical between say 6800 A and 8000 A. 7000 A is about the optimum.

G. Determination of Blanks

1. Cell to Cell Blanks

When both sample and distilled water cells are filled with distilled water the extinction of one against the other should be 0.000. Due to slight optical defects a slight positive or negative value may be found. The water in the distilled water cell should be changed every day as marked turbidities can result even in distilled water if it remains in the cell for too long.

2. Reagent Blank

The amount of phosphorus in the perchloric acid reagent is very small and variations in the amount of this acid used may be neglected. A blank determination is only necessary when a new batch of perchloric acid, ammonium molybdate or dilute ammonia are used and should not exceed about 0.05. It should be checked every few days, in duplicate, during a run of analyses.

Place 8 ml. of Reagent No. 1 and 2 to 3 drops of Reagent No. 2 into a conical flask and add about 1 to 2 ml. of synthetic sea water (see Section H). This addition provides a little solid in the flask to minimize volatilization of phosphorus but contributes a negligible blank. Evaporate, without coverglass, until solid separates and only a few tenths of a ml. of perchloric acid remains. Cool somewhat, add 5 ml. of dilute ammonia solution, Reagent No. 3, and evaporate to dryness but do not bake. Continue exactly as described in Section F paragraphs 5-7 and correct the resulting extinction for any cell to cell blank.

3. Preliminary Cleaning of Glassware

Clean pyrex Erlenmeyer flasks have been found to give no phosphate contamination. Flasks should be retained especially for the present method and not put into general circulation. Before their initial use, they should be boiled to fumes after adding about 30 ml. of water, 20 ml. of concentrated hydrochloric acid and 10 ml. of Reagent No. 1. The perchloric acid is then refluxed vigorously in each flask for about one hour. A blank determination (G.2. above) should then be carried out on each flask before it is finally put into use. The flasks are rinsed thoroughly with distilled water after each determination and stored dry. The capillary antibump devices and the 2-inch coverglasses should be boiled for a few minutes in 50 per cent V/V hydrochloric acid solution before use or after a prolonged shut-down period.

H. Calibration

1. Standard Phosphate Solution

Dissolve 0.340 g. of anhydrous potassium dihydrogen phosphate, KH_2PO_4, in 1000 ml. of distilled water. Store in a dark bottle with 1 ml. of chloroform. The solution is stable for many months.

1 ml. $\equiv$ 2.5 μg.at.P.

Dilute 10.0 ml. of this solution to 1000 ml. with distilled water. Store in a dark bottle with 1 ml. of chloroform. The solution should be stable for many weeks but, for safety, should be made afresh about once every 10 days.

1 ml. $\equiv$ 2.5×10^{-2} μg.at.P.

1 ml. $\equiv$ 0.50 μg.at.P./l. in 50 ml. of seawater sample.

2. Synthetic Sea Water

Dissolve 25 g. of analytical reagent quality sodium chloride, NaCl, and 8 g. of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, in each liter of distilled water. This solution is best made up in 5 - 20 liter quantities at a time and stored in polyethylene. The phosphorus blank extinction on this solution should not exceed 0.1 - 0.15 initially.

3. Procedure

The evaporation and fuming procedure described in this method result in a slight, but reproducible, loss of phosphorus which may amount to several per cent. If fuming is taken to dryness the loss approaches 15 per cent. The explanation for this is obscure but it appears as if phosphoric acid must co-distill with perchloric acid vapour despite the very large differences of vapour pressure at around 300° C. For safety, therefore, it is best to calibrate each batch of samples by taking standards throughout the entire method.

Add 50 ml. of synthetic sea water to each of five flasks. Reserve two

flasks as blank determinations and to each of the three others add 6.0 ml. of the dilute phosphate solution (equivalent to 3 μg.at.P./l. on 50 ml.). Add 8.0 ml. of Reagent No. 1 to each flask and carry these standards and blanks through the full method as described in Section F paragraphs 2-7 inclusive. For colour development the standards should be placed in the middle of each batch of samples.

Calculate the factor F from the expression:

$$F = \frac{3.00}{E_s - E_b}$$

where E_s is the mean extinction of the three standards and E_b is the mean extinction of the two blanks (not corrected for cell to cell blanks). The value of F should be between about 3.5 and 4.

Note. The factor F, as determined here, may be a little lower than the factor found in Standard Method No. P. 1.A. as no chlorides are present. The perchlorates and sulphates present after fuming with perchloric acid give less suppression of the colour than is found with an equivalent amount of untreated sea water.

Approved December 1957 Standard Method No. P. 2.A

Addendum No. 1

DETERMINATION OF TOTAL PHOSPHORUS IN SEA WATER

(AND ORGANIC PHOSPHORUS BY DIFFERENCE)

Addition to Section E

It appears to be impossible to prevent a very small, but detectable, pick-up of phosphorus from glassware over a sufficient period of time but pyrex boiling tubes, 200 mm. x 25 mm. holding about 80-90 ml., have proved satisfactory for storing samples for total phosphate for a period exceeding a month. The tubes are cleaned thoroughly in hot chromic-sulphuric acid for several hours, rinsed thoroughly with distilled water and conditioned by being allowed to stand full of slightly acidic water (1 drop of concentrated hydrochloric acid) for several months. When not in use the tubes should be kept nearly full of acidic water and covered with a clean square of Parafilm. In no circumstances should a cork or rubber stopper be used as either can introduce contamination. This water is emptied, and the tube drained as dry as possible, immediately before 50 ml. of sample are placed in it for storage on the ship. One to 2 drops of concentrated hydrochloric should be added to each sample to acidify the seawater sample during storage, and the tubes should be re-stoppered by Parafilm sheeting. The very slight phosphorus pick-up which may still occur during a cruise (ca. 0.1 μg.at.P/l.) can be minimized by storing tubes in a deep-freeze and by assessing a mean blank correction. This is obtained by storing synthetic sea water of known total phosphorus content in 3 to 4 tubes selected at random and redetermining the total phosphorus

at the end of the cruise.

Addition to Section F

(ca. 0.1 μg.at.P/l.) The extinction of samples should not exceed 1.5, equivalent to about 6 μg.at.P/l., or readings may be in appreciable error owing to optical defects in the spectrophotometer used. If extinction values exceed about 1.2 the slit width of the Beckman DU Spectrophotometer should be increased to 0.05 mm. to allow greater sensitivity of response in the instrument.

For quantities of phosphorus exceeding about 5 μg.at.P/l. the six minutes reduction time, Standard Method No. P. 2.A, Section F. 7, is too near the safe upper limit and the reduction time should be reduced to 4 minutes. (For 7 μg.at.P/l. the stable maximum extinction persists from 2.5 to 6.0 minutes at 23° C.) Occasionally total phosphorus extinction values may exceed 1.5. When this occurs dilute 25 ml. of the reduced solution to 50 ml. in a stoppered graduated 50 ml. measuring cylinder by pouring the sample into a cylinder containing exactly 25 ml. of distilled water. Mix and re-measure the extinction at once. If this final extinction measurement is made no longer than 6 minutes after the addition of stannous chloride the extinction obtained after dilution may be doubled to give the correct initial extinction value. In this manner the maximum total phosphorus that can be determined by Standard Method No. P. 2.A is extended to about 8 μg.at.P/l.

Correction to Section A

At the top of page 67 $\pm \frac{0.16}{n}$ should read $\pm \frac{0.16}{n^{1/2}}$.

Approved June, 1957 Standard Method No. Si. 1.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF SOLUBLE SILICATE IN SEA WATER

(File N 7-1-5 June 30, 1957)

A. Capabilities of the Method

Range 0.1 - 140 μg. atoms Si./liter

The following data are based on a statistical treatment of the results obtained by trained operators in a shore-base laboratory. Statistics under sea-going conditions are awaited, but the precision is not expected to be worse by a factor exceeding about 1.5.

1. Precision at 100 μg.at.Si./l Level

The correct value lies in the range: Mean of n determinations $\pm \frac{2.5}{n^{1/2}}$ μg.at.Si./l. (Determined using 1 cm. cells.)

2. Precision at 10 μg.at.Si./l Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.25}{n^{1/2}}$ μg.at.Si./l. (Determined using 10 cm. cells.)

3. Limit of Detection

The smallest amount of silicate that can be detected with certainty is about 0.1 μg.at.Si./l.

Reject duplicate determinations if the extinction* values differ by more than 0.05. in the extinction range 0.5 -.1.0 on a 1 cm. cell,
or more than 0.025 in the extinction range 0.1 - 0.5 on a 1 cm. cell,
or more than 0.05 in the extinction range 0.5 - 1.0 on a 10 cm. cell.

If duplicate extinction values differ by less than the above limits, take a mean value.

Note. The above statistical data apply at the 0.05 probability level, i.e., the odds are 19 to 1 in their favour.

B. Outline of Method

The sea water sample is allowed to react with molybdate under conditions which result in the formation of the silicomolybdate, phosphomolybdate and arsenomolybdate complexes. A reducing solution, containing metol and oxalic acid, is then added which reduces the silicomolybdate complex to give a blue reduction compound and simultaneously decomposes any phospho or arsenomolybdate, so that interference from phosphate and arsenate is eliminated. The extinction of the resulting solution is measured using 1 cm. or 10 cm. cells and light of wavelength near to 8100 A.

C. Special Apparatus and Equipment

A Beckman DU Spectrophotometer or any other seaworthy spectrophotometer

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* The extinction, E, is defined as $\log_{10}\frac{I_o}{I}$, where I_o and I are the incident and transmitted light intensities, respectively. The Beckman DU Spectrophotometer is calibrated directly in extinction units. If the absorptiometer employed reads per cent transmission, T, calculate E as $\log_{10}\left(\frac{100}{T}\right)$.

capable of measuring the extinction of light of wavelength near to 8100 A.

If the most precise values are needed for amounts of silica less than about 12 μg.at.Si./l, then spectrophotometer or absorptiometer cells having a path length of 10 cm. and holding less than 40 ml. of solution should be available.

Fifty ml. capacity stoppered graduated glass measuring cylinders, one for each silicate determination.

Two polyethylene wash bottles, one of at least 300 ml. capacity.

D. Special Reagents Required

1. Molybdate Reagent (Reagent No. 1)

Dissolve 4.0 g. of analytical reagent quality ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (preferably finely crystalline) in about 300 ml. of distilled water. Add 12.0 ml. of concentrated hydrochloric acid (12 N s.g. 1.18), mix and make the volume to 500 ml. of distilled water. Store the solution in a polyethylene bottle in which it is stable for many months provided that it is kept out of direct sunlight.

2. Metol-Sulphite Solution

Dissolve 6 g. of anhydrous sodium sulphite in 500 ml. of distilled water and then add 10 g. of metol (p-methylaminophenol sulphate). When the metol has dissolved filter the solution through a No. 1 Whatman filter paper into a polyethylene bottle. The solution is stable for many months provided that the bottle is tightly stoppered but should be discarded if a very pronounced brown colouration develops.

3. Oxalic Acid Solution

Prepare a saturated oxalic acid solution by shaking 50 g. of analytical reagent quality oxalic acid dihydrate with 500 ml. of distilled water. Decant

the solution from the crystals for use. This solution may be stored in a glass bottle and is stable indefinitely.

4. Sulphuric Acid Solution 50 Per Cent V/V

Pour 250 ml. of concentrated (s.g. 1.82) analytical reagent quality sulphuric acid into 250 ml. of distilled water. Cool to room temperature and make the volume to 500 ml. with a little extra water.

5. Reducing Reagent (Reagent No. 2)

Mix 100 ml. of metol-sulphite solution with 60 ml. of oxalic acid solution. Add slowly, with mixing, 60 ml. of 50 per cent V/V sulphuric acid solution and make the mixture to a volume of 300 ml. with distilled water. This solution should be prepared for immediate use. It may be kept for up to a week in the dark in a glass or polyethylene bottle, provided that the bottle is tightly stoppered.

E. Sampling Procedure and Sample Storage

Samples of sea water should not be stored in glass bottles for more than a few minutes prior to analysis and it is best, therefore, to transfer samples directly into waxed glass or into polyethylene containers. To minimize the effect of diatom multiplication store samples in the dark and for no longer than a day prior to analysis. Storage of low plankton waters is feasible for a few weeks if samples are kept at or near to 0° C but some suspended siliceous matter dissolve and cause an appreciable error if the storage period exceeds a fortnight.

F. Experimental

Procedure

1. Sample solutions should be at a temperature between about 18° C and

25° C (note a). Add 10 ml. of molybdate solution (Reagent No. 1) to a dry 50 ml. measuring cylinder, fitted with a stopper (note b). Pipette 25 ml. of sea water sample into the cylinder, stopper, mix the solutions and allow the mixture to stand for 10 minutes (notes c and d).

2. Add the reducing reagent (Reagent No. 2) rapidly so as to make the volume exactly 50 ml. (note b) and mix immediately (note e).

3. Allow the solution to stand for 1-2 hours (note f) to complete the reduction of the silicomolybdate complex (note g). If precise values are required on amounts of silicon below about 12 μg.at.Si./l use a 10 cm. cell, otherwise measure the extinction of the solution in a 1 cm. cell against distilled water. A wavelength of 8100 A and a slit width of 0.03 mm. should be used with the Beckman DU spectrophotometer (red sensitive photocell). If a filter-type absorptiometer is used chose a filter having a maximum transmission above 7000 - 8000 A (note h). Record extinction values (and corrected values, see 4, below) to the nearest 0.001 unit in the range 0.000 - 0.200, to the nearest 0.0025 unit in the range 0.200 - 0.400 and to the nearest 0.005 for extinction values exceeding 0.400. Unless adjacent samples are known to have extinction values within about 25 per cent of each other the absorptiometer cell should be rinsed with each new solution before filling.

4. Correct the measured extinction by subtracting a reagent blank obtained with a 1 cm. or 10 cm. cell as appropriate (see Section G). Calculate the soluble silicate concentration in microgram atoms of silicate silicon per liter (μg.at.Si./l) from the expression:

$$\mu g.at.Si./l = \text{corrected extinction} \times F$$

Where F is a factor for each length of cell, obtained as described in Section H below. Report results to three significant figures. Neither phosphate nor arsenate interfere with this method.

Notes

a. There is no pronounced temperature effect with this method but samples, especially at the reduction stage, should be at a temperature exceeding about 18° C. Temperatures exceeding 25 - 30° C must be avoided as this hastens the decomposition of the silicomolybdate complex.

b. The ammonium molybdate should be measured directly to about ± 0.5 ml. in the cylinder being used. At sea this reagent, and the reducing reagent (see 2) are conveniently dispensed from polyethylene wash bottles.

c. The silicate and molybdate must combine before the reducing agent is added. Ten minutes is allowed for this reaction. The addition of the reducing solution must not be delayed for more than a further 30 minutes or else undesirable changes in the isomeric form of the silicomolybdate complex will take place.

d. The sample is added to the acid molybdate reagent, rather than in the reverse order, so that the sea water-molybdate mixture is always above a certain acidity. This prevents the possible formation of an undesirable isomeric form of the silocomolybdate complex.

e. The use of a metol reductant results in a less sensitive method than is found when stannous chloride is used. However, sensitivity is not of prime importance with silicon, which is relatively abundant in sea water in comparison with an element such as phosphorus, and the metol reagent has some advantages. The reagent is more stable than stannous chloride and the long-term stability of the blue colour formed is much greater when metol is used. As yellow pentavalent molybdenum compounds are not produced the procedure for estimating the "blank" correction is much less complicated than is the case when stannous chloride is employed. Oxalic acid is added to the reducing reagent to decompose any phospho or arsenomolybdate formed along

with the silicomolybdate complex.

f. The time required for full formation of the blue colour varies a little with the amount of silicon being determined. With less than about 50 μg.at.Si./l one hour is sufficient. For amounts exceeding 75 - 100 μg.at.Si./l, however, only some 95 per cent of the silicomolybdate complex may be reduced in 60 minutes and, for safety, at least 1 1/2 - 2 hours should be allowed. A very slight increase (1 - 2 per cent) may be recorded in the next 12 - 24 hours but the effect can be neglected. Solutions are, for all practical purposes, stable for 12 hours.

g. The dependence of extinction on salinity is discussed in Section H, below.

h. Unless the absorptiometer is sensitive to the near infra-red a marked reduction in the sensitivity of this method can be expected. The effect is not serious for wavelengths exceeding 6500 A but a slight deviation from the Beer-Lambert Law may necessitate the use of calibration curves.

G. Determination of Blanks

Normally the effect of sea water turbidity may be neglected but if precise values for amounts of silicon less than 5 - 10 μg.at.Si./l are required on turbid waters (using 10 cm. cells) a turbidity correction should be applied (see, for example, Standard Method No. P. 1.A., Section G).

The blank correction for distilled water stored in polyethylene may be considered negligible, and a satisfactory blank for the reagents is obtained by using distilled water to replace the sea water.

Carry out the method exactly as described in Section F, paragraphs 1 - 3 inclusive, using 25 ml. of distilled water in place of the sea water sample. This blank should not exceed about 0.01 on a 1 cm. cell or 0.1 on a 10 cm. cell and should be measured for each batch of reagents and checked

at weekly intervals during a cruise. If 10 cm. cells are used the blank should be determined, in duplicate, with each batch of samples.

H. Calibration

1. Standard Silicate Solution

Ignite about 0.5 g. of chromatographic powdered silicic acid in a platinum dish for one hour at 1000° C. Cool in a desiccator. Weigh out 0.150 g. of the resulting anhydrous silica into a platinum crucible and add 1 g. of anhydrous sodium carbonate, Na_2CO_3. Mix the solids with the tip of a clean dry nickel spatula and fuse gently over a bunsen burner until the melt is quiet. Finally hold the melt at 1000° C in a muffle furnace for a few minutes until it is quite clear. Cool and extract quantitatively in a little hot water. Make the resulting solution to exactly 500 ml. in a measuring flask and transfer the solution immediately to a polyethylene bottle. The standard is stable indefinitely.

1 ml. ≡ 5 µg.at.Si.

Dilute 10 ml. of this solution to 500 ml. with synthetic sea water (see below). Use this solution at once for calibration purposes. If a delay of more than a few hours is necessary the solution should be transferred to a plastic container.

1 ml. ≡ 0.1 µg.at.Si.

1 ml. ≡ 4 µg.at.Si./l in 25 ml. of sea water sample.

2. Synthetic Sea Water

Dissolve 25 g. of analytical reagent quality sodium chloride, NaCl, and 8 g. of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$ in each liter of distilled water. This water is equivalent, for analytical purposes to sea water of salinity 28 °/₀₀. This solution is best made up in 5 - 20 liter quantities

at a time and must be stored in a polyethylene container. The silicon content of this solution should not exceed 1 - 2 μg.at.Si./l.

3. Procedure

Carry out the silicon determination as described in Section F, above, (paragraphs 1-3) using 25 ml. of the silicon standard (dilute) instead of a sea water sample. Determine the extinction of six such standards and of two blanks made with synthetic sea water. A reagent blank is unnecessary. Measure the extinction in a 1 cm. cell after allowing at least 2 hours for full colour development (see note f).

Calculate the factor $F_{1\ cm.}$ from the expression:

$$F_{1\ cm.} = \frac{100}{E_s - E_b}$$

where E_s is the mean extinction of the six standards and E_b is the mean extinction of the two blanks. The value for $F_{1\ cm.}$ should not change and requires checking only infrequently at the discretion of the analyst. The value should be very close to 100. If a 10 cm. cell is used, for the most precise estimate of low amounts of silicate (less than about 12 μg.at.Si./l), the factor $F_{10\ cm.}$ is equal to 0.1 x $F_{1\ cm.}$

Note. The factor F is a function of the salinity of sea water samples. Between salinities 25 °/₀₀ and 35 °/₀₀ the variation is less than 3 per cent and may be neglected. The factor F_s at a salinity S °/₀₀ is related to the factor, F, obtained as described above by the approximate formula:

$$F_s = \frac{F \times (1 + 0.003.S)}{1.08}$$

This correction should be used for the most precise work when the salinity varies by more than about 10 °/₀₀ from a value of 28 °/₀₀. The factor for pure water (zero salinity) is thus some 7 per cent less than the value obtained by the present method using synthetic sea water.

Approved June, 1957 Standard Method No. N. 1.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF NITRITE IN SEA WATER

(File N 7-1-5 June 30, 1957)

A. Capabilities of the Method

Range 0.01 - 2.5 μg. atoms N/liter

The following data are based on a statistical treatment of the results under sea-going conditions by trained operators using the procedure exactly as described.

1. Precision at 1 μg.at.N./l. Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.032}{n^{1/2}}$ μg.at.N./l.

2. Precision at 0.3 μg.at.N./l. Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.023}{n^{1/2}}$ μg.at.N./l.

3. Limit of Detection

The smallest amount of nitrite nitrogen that can be detected with certainty is 0.01 μg.at.N./l.

Reject duplicate determinations if the extinction* values differ by

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* The extinction, E, is defined as $\log_{10} \frac{I_o}{I}$, where I_o and I are incident and transmitted light intensities, respectively. The Beckman DU Spectrophotometer is calibrated directly in extinction units. If the absorptiometer employed reads per cent transmission, T, calculate E as $\log_{10}\left(\frac{100}{T}\right)$.

more than 0.03 in extinction range 0.5 - 1.0

or more than 0.02 in extinction range 0.1 - 0.5

or more than 0.005 in extinction range 0.03 - 0.1.

If the duplicate extinction values differ by less than the above limits, take a mean value.

Note. The above statistical data apply at the 0.05 probability level, i.e. the odds are 19 to 1 in their favour.

B. Outline of Method

The nitrite in the sea water is allowed to react with the aromatic amine, sulphanilamide, in an acid solution. The resulting diazo compound reacts with N(1-napthyl) ethylene diamine and forms a highly coloured azo dye the extinction of which is measured using 10 cm. cells and light of wavelength near to 5400 A.

C. Special Apparatus and Equipment

A Beckman DU Spectrophotometer or any other seaworthy spectrophotometer capable of measuring the extinction of light of wavelength near to 5400 A.

Spectrophotometer or absorptiometer cells having a path length of at least 10 cm. and holding less than 40 ml. of solution.

D. Special Reagents Required

1. Sulphanilamide Reagent (Reagent No. 1)

Dissolve 5 g. sulphanilamide in 50 ml. of concentrated hydrochloric acid (s.g. 1.18) and dilute the solution to 500 ml. with distilled water. This solution is stable for many months.

2. N(1-napthyl) Ethylene Diamine Dihydrochloride Reagent (Reagent No. 2)

Dissolve 0.50 g. of the dihydrochloride in 500 ml. of distilled water.

Store the solution in a dark bottle. The solution is stable for many weeks but should be renewed if the blank (see Section G) becomes too high.

E. Sampling Procedure and Sample Storage

The 50 ml. measuring cylinder and 125 ml. conical pyrex flasks used for this determination should be rinsed twice with the sample, drained by inverting and shaking and then 50 ml. of sample measured into the flask. Samples are stable in subdued light for many hours at room temperature but the analysis should not be delayed for more than about 5 - 10 hours. If greater delays are unavoidable the samples should be frozen. Withdraw a separate sample of about 20 ml. for turbidity measurement unless this is to be obtained in a simultaneous phosphate or other determination.

F. Experimental

Procedure

1. Measure the extinction of samples to obtain the turbidity correction. (See 3 below for the necessary precision of measurement. See Section G.3 for further details.)

2. Add 1.0 ml. of sulphanilamide solution (Reagent No. 1) from an automatic pipette to each sample (50 ml. in a 125 ml. conical flask), mix, and allow the reagent to react for a period greater than 2 minutes but not exceeding 8 minutes (notes a and b).

3. Add 1.0 ml. of napthylethylene diamine solution (Reagent No. 2) and mix immediately. Between 10 minutes and 2 hours afterwards measure the extinction of the solution in a 10 cm. cell against distilled water (note c). A wavelength of 5430 A and slit width of 0.03 mm. should be used with the Beckman DU Spectrophotometer (blue sensitive photocell).

If a filter-type absorptiometer is used choose a filter having a peak

transmission as near to 5400 A as possible. Record extinction values (and corrected values, see 4 below) to the nearest 0.001 unit in the range 0.000 - 0.200, to the nearest 0.0025 unit in the range 0.200 - 0.400 and to the nearest 0.005 for extinction values exceeding 0.400. Unless adjacent samples are known to have extinction values within about 25 per cent of each other, the absorptiometer cell should be rinsed with each new solution before filling.

4. Correct the measured extinction by subtracting both turbidity and reagent blanks (see Section G). Calculate the nitrite nitrogen concentration in micro-gram atoms of nitrogen per liter (μg.at.N./l) from the expression:

$$\mu\text{g.at.N./l} = \text{corrected extinction} \times F$$

where F is a factor obtained as described in Section H below. Report results to three significant figures. Numerous compounds can interfere with this method, but none of them will be present in significant amounts in ocean, inshore or estuarine waters.

Notes

a. This method is not appreciably affected by salinity, small changes in reagent concentration and volume or by temperature. The latter, however, should be within the range of about 15° C to 25° C. The exact volume of sample is not critical but should lie between 45 and 55 ml.

b. The diazotising reaction requires 2 minutes for completion, but undesirable side reactions and decomposition become significant after about 10 minutes.

c. Ten minutes is required for complete colour development. The colour is stable for at least two hours but slowly fades thereafter. A 2-hour maximum is a safe limit.

G. Determination of Blanks

1. Cell to Cell Blanks

When both sample and distilled water cells are filled with distilled water the extinction of one against the other should be 0.000. Due to slight optical defects, a slight positive or negative value may be found. This is allowed for when turbidity blanks are subtracted (see below) but the value should be found when determining the reagent blank. The water in the distilled water cell should be changed every day as marked turbidities can result, even in distilled water, if it remains in the cell for too long.

2. Reagent Blanks

Carry out the method exactly as described in Section F, paragraphs 2 and 3 inclusive, using distilled water in place of sea water. Correct the resulting extinction for the cell to cell blank. The reagent blank should not exceed 0.03. The origin of this blank is obscure. It appears to arise mainly when both reagents are mixed and changes somewhat from day to day. It should be determined (mean of duplicates) for each batch of samples.

3. Seawater Turbidity Blanks

These may be a very appreciable fraction of the total extinction which rarely exceeds 0.3 in nitrite determinations. Turbidity blanks should be determined on the surface and 10 m. samples of each cast. Measure at progressively greater depths until the value becomes appreciably constant. This value (generally less than 0.01 at below 25 m. in offshore waters) is then roughly equal to the cell to cell blank (Section G.1 above) and may be slightly negative. For the most precise work, turbidity blanks should be measured on separate 20 ml. samples of the sea water concerned, but it is normally sufficient to take the values used for phosphate or other determinations if these have

been measured within a few hours of the nitrite determinations.

H. Calibration

1. Standard Nitrite Solution

Anhydrous analytical reagent quality sodium nitrite, $NaNO_2$, is sufficiently pure for calibration purposes. For safety a little of the salt should be dried at 110° C for an hour. Dissolve 0.345 g. in 1000 ml. of distilled water. Store the solution in a dark bottle with 1 ml. of chloroform as a preservative. The solution is stable for at least 1 to 2 months.

$$1 \text{ ml.} \equiv 5 \ \mu\text{g.at.N.}$$

Dilute 10.0 ml. of this solution to 1000 ml. with distilled water and use the same day.

$$1 \text{ ml.} \equiv 5 \times 10^{-2} \ \mu\text{g.at.N.}$$

$$1 \text{ ml.} \equiv 1.0 \ \mu\text{g.at.N./l in 50 ml. of seawater sample.}$$

2. Procedure

Prepare four standard solutions consisting of 2.00 ml. of the dilute nitrite solution (measured with a 2.00 ml. graduated pipette) made to a volume of 50 ml. in a graduated flask or 50 ml. measuring cylinder. Transfer the solutions to four dry 125 ml. conical flasks and place 50 ml. of distilled water in two more flasks to act as blanks. Carry out the nitrite determination as described in Section F above (paragraphs 2-3).

Calculate the factor F from the expression:

$$F = \frac{2.00}{E_s - E_b}$$

where E_s is the mean extinction of the four standards and E_b is the mean extinction of the two blanks (not corrected for cell to cell blanks).

Note. The factor F does not vary with time or over a wide range of experimental

conditions and is near to 2.1 when the Beckman DU Spectrophotometer is employed. For safety it should be checked before the use of any new batch of reagents, or before each cruise.

Approved July, 1957 Standard Method C. 1.A.

FISHERIES RESEARCH BOARD OF CANADA

Pacific Oceanographic Group
Nanaimo, B.C.

DETERMINATION OF CARBONATE, BICARBONATE AND FREE CARBON DIOXIDE IN SEA WATER FROM PH AND ALKALINITY MEASUREMENTS

(File N 7-1-5 July 15, 1957)

Definitions cf. Addendum No. 1, page 110.

1. Total Alkalinity

Titration alkalinity is the number of milliequivalents of hydrogen ion that are neutralized by one kg. of sea water at 20° C when a large excess of acid is added. This approximates closely to the acid required to titrate a solution to the pH inflection point near pH 4.5. The total alkalinity is often expressed per liter (20° C) rather than per kg. and the difference of 2 to 3 per cent is rarely significant. A volume basis is used in the tables and equations in the present method.

2. Specific Alkalinity

This is defined as the ratio:

$$\frac{\text{total alkalinity (kg. basis)}}{\text{Cl °/}_{\text{oo}}} = \frac{\text{total alkalinity (liter basis)}}{\text{Cl/l.}_{20^\circ\text{ C}}}$$

and approximates to 0.125. The ratio may vary appreciably, however, according to the nature of the water mass concerned and must be determined experimentally for the most precise work.

3. Carbonate Alkalinity

The number of milliequivalents of hydrogen ion that are neutralized by one kg. of sea water (or one liter at 20° C in the present method) in converting

carbonate and bicarbonate ions to carbon dioxide by the reactions:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^{1-}$$

$$HCO_3^{1-} + H^+ \rightleftharpoons H_2CO_3$$

In all natural sea waters, with a salinity exceeding about 10 °/₀₀ - 15 °/₀₀, the total alkalinity will arise from the ions CO_3^{2-}, HCO_3^{1-}, $H_2BO_3^{1-}$, OH^{1-} and, in a negative sense, H^+. The effect of other ions can be neglected. Therefore, by definitions, if [ ] represents concentration in millimoles per liter:

$$\underline{\text{Total alkalinity}} = \left[HCO_3^{1-}\right] + 2\left[CO_3^{2-}\right] + \left[H_2BO_3^{1-}\right] + \left[OH^{1-}\right] - \left[H^+\right]$$

$$\underline{\text{Carbonate alkalinity}} = \left[HCO_3^{1-}\right] + 2\left[CO_3^{2-}\right]$$

Whence:

$$\underline{\text{Carbonate alkalinity}} = \text{total alkalinity} - \left[H_2BO_3^{1-}\right] - \left[OH^{1-}\right] + \left[H^+\right]$$

The terms $\left[OH^{1-}\right]$ and $\left[H^+\right]$ may be neglected in the pH range 5.3 - 8.7.

The term $\left[H_2BO_3^{1-}\right]$ may only be neglected at pH values less than 7.3.

PART I. DETERMINATION OF EXPERIMENTAL QUANTITIES

1. pH Determination

Range pH 7.3 - pH 8.8

A. Capabilities of the Method

The equipment and conditions used are so varied that no general statement can be made. If the pH is used as a general indicator of water masses and water structure a precision of ± 0.03 unit is probably sufficient and should be easily obtainable.

For measurements designed to be used in the calculation of the total carbon dioxide content of sea water a precision of ± 0.02 unit should be attempted and can be obtained under sea-going conditions if care is taken.

For measurements designed to be used in the calculation of the relative amounts of the various forms of carbon dioxide (CO_3^{2-}, HCO_3^{1-} and free CO_2) the highest possible precision is required in pH measurement. Ideally a precision of ± 0.005 unit should be attempted but under most conditions it is doubtful whether better than ± 0.01 can be achieved and then the greatest care in sampling and standardizations is required.

B. Outline of Method

The pH of a sample is measured by a glass electrode and electrometer type pH meter after taking certain precautions in sampling and standardization. The pH is measured at laboratory temperature and pressure and the pH of the sea water, in situ, is derived by calculations involving a knowledge of the temperature and pressure of the sample when taken.

C. Special Apparatus and Equipment

For the most precise work a Beckman Model G pH meter, or an instrument of similar specification, should be employed with "wide range" (-5° C to 80° C,

pH 0 to 11) glass electrodes and saturated calomel half-cell electrodes. Automatic reading instruments are satisfactory for shipboard use, where a precision of about ± 0.03 unit is acceptable.

Fifty ml. wide-mouth screw-capped polyethylene bottles for each sample.

D. Special Reagents Required

Standard Buffer

0.025 M. KH_2PO_4 + 0.025 M. Na_2HPO_4. pH 6.87 at 20 - 25° C

Dissolve 34.0 g. of potassium phosphate (monobasic), KH_2PO_4, and 35.5 g. of anhydrous sodium phosphate (dibasic), Na_2HPO_4, in distilled water and make the volume to 1000 ml. in a measuring flask. Store in a tightly-stoppered glass bottle.

Dilute 100 ml. of this solution to 1000 ml. with distilled water for use. The dilute solution should be stored in polyethylene and is stable for many weeks if evaporation is prevented.

E. Sampling Procedure and Sample Storage

Samples must be warmed to laboratory temperature before measurement and this should occur with the minimum exchange of atmospheric and dissolved carbon dioxide. In no circumstances must the delay in measuring the pH exceed 1 to 2 hours. The sample should be taken from reversing bottles immediately after the oxygen sample (Standard Method No. O. 1.A.) by filling a 50 ml. wide-mouth (27 mm. in diameter or greater) polyethylene bottle to the brim and closing it at once with a tight-fitting screw cap.

If thin, probe-type, electrodes are available, which may be inserted in an opening of 12-15 mm. diameter, the samples may be collected in 30 or 50 ml. polyethylene narrow-mouth screw-capped bottles, filled to the brim.

F. Experimental

Measure the temperature of the buffer solution (see Section D) to the nearest 1° C, adjusting it, if necessary, so that the temperature lies between 20° C and 25° C. Set the temperature compensator of the pH meter to this temperature and the pH to read 6.87 and standardize the instrument according to the maker's instructions allowing 5 minutes for the electrodes to reach equilibrium. The pH of the buffer is constant in the temperature range 20° C to 25° C and a standardization at pH 6.87 will be effective for the pH range 7-9. With a satisfactory meter and electrodes the standardization need be repeated only once or twice a day.

Place the samples in a water bath, preferably thermostatically controlled, until they attain a temperature within ± 3° C of the temperature at which the pH meter was standardized. (If the temperature of samples and buffer differ by more than 3° C errors may become appreciable as the temperature compensator on the pH meter does not effect a complete temperature correction.)

If the electrodes have just been immersed in buffer they should be washed with water and gently dried with a little paper tissue, otherwise the electrodes are transferred from one solution to another without rinsing or wiping. Remove the cap from the sample bottle and immerse the glass and calomel electrodes well down into the bottle. Measure the pH and temperature of the sample after not less than 3 minutes and not longer than 5 minutes immersion, adjusting the temperature compensator of the meter to the solution temperature just before a final reading is taken. The solution should be gently swirled once or twice to assist the electrodes in reaching equilibrium.

Note the pH and the temperature of the solution, pH_m and t_m, respectively. If the sample was initially at a temperature, t° C, when taken at a

depth d meters, its correct pH, *in situ*, is given by the expression:

$$pH_s = pH_m - x(t - t_m)$$

neglecting pressure effects. The latter are rarely significant but the pH at depth d meters, pH_d, is related to the pH at the surface, pH_s, by the expression:

$$pH_d = pH_s - y.d.$$

Values for the coefficients x and y are given in PART III, Tables IA and IB. The temperature correction should always be applied before making the calculations described in PART II. The pressure variation is negligible for samples taken above about 500 m.

2. Total Alkalinity Determination

Range 0 - 2.8 milliequivalents per liter

A. Capabilities of the Method

The following data are based on a statistical treatment of the results obtained in a shore-base laboratory by trained operators using the procedure exactly as described and a direct reading Beckman Model H2 pH meter. A slightly improved precision should be possible using a Beckman Model G meter.

1. Precision at the 2.0 Milliequivalents Total Alkalinity Level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.022}{n^{1/2}}$ milliequivalents total alkalinity per liter.

Reject duplicate determinations if the pH values after acidification (see below) differ by more than: 0.02 at the pH 3.0 level.
0.04 at the pH 3.5 level.
0.08 at the pH 4.0 level.

B. Outline of Method

One hundred ml. of sea water sample are mixed with 25 ml. of exactly 0.0100 N hydrochloric acid. The pH of the resulting solution is measured. The standard acid in excess of that required to titrate the sample to the carbon dioxide inflection point is computed from a knowledge of this pH and an empirical factor. This excess acid is then subtracted from 2.500 milliequivalents/l (the amount initially added by 25 ml. of 0.01 N acid) and the total alkalinity of the sample is thus evaluated.

C. Special Apparatus and Equipment

For the most precise work a Beckman Model G pH meter, or an instrument of similar specification, should be employed with "wide range" (-5° C to 80° C,

pH 0 to 11) glass electrodes and saturated calomel half-cell electrodes. Automatic reading instruments are only acceptable if used with the greatest possible precision (± 0.025 unit or better).

Two hundred ml. wide-mouth screw-capped polyethylene bottles for each sample.

D. Special Reagents Required.

1. Standard 0.01000 N Hydrochloric Acid.

Prepare 0.01000 N hydrochloric acid by standardizing acid of a slightly greater concentration and then adjusting the volume by the addition of a calculated amount of distilled water to bring the normality to precisely 0.1000 N. Dilute this solution exactly ten fold, by a pipette and measuring flask, before use.

2. Standard Buffer

0.05 M. Potassium Hydrogen Phthalate

Dissolve 10.21 gm. of analytical reagent quality (primary buffer standard specification) potassium hydrogen phthalate, $KHC_8H_4O_4$, in distilled water and make the volume to 1000 ml. in a measuring flask. Store in a glass bottle. The solution is stable in the absence of evaporation and the formation of a slight turbidity introduces no error.

E. Sampling Procedure and Sample Storage

No great problems are encountered in sampling and storage. The samples are best stored in plastic or in glass bottles that have been soaked for several days in one per cent hydrochloric acid and then rinsed thoroughly in distilled water before they are dried. Evaporation must be prevented by tightly stoppering the containers and it is best to carry out the determinations on the same day as the samples are taken by pipetting the seawater sample directly into

standard acid, (see Section F). However, careful storage of the samples for several weeks, as for salinity (see Standard Method No. Sal. 1.A), is permissible.

F. Experimental

Pipette 25.0 ml. of standard 0.01000 N hydrochloric acid into a dry 200-ml. polyethylene wide-mouth screw-cap bottle. Add from a pipette 100.0 ml. of seawater sample. Stopper the bottle and mix the solutions thoroughly. Warm the solution to room temperature and measure the pH exactly as described in PART I 1.E. above, except use the phthalate buffer to standardize the pH meter instead of the phosphate buffer. The pH of the phthalate buffer between 20° C and 25° C is taken as 4.00.

G. Calculations

1. Find the value of a_H corresponding to the measured pH value from Table II. The pH must lie in the range 2.8 - 4.0. (As the pH is measured in the range 20° C to 25° C no temperature correction is necessary.)

2. Find the value of f from Table III, according to the salinity and pH value.

3. Calculate the total alkalinity from the equation:

$$\text{Total alkalinity} = 2.500 - 1250\left(\frac{a_H}{f}\right)$$

Note 1. For chlorinity values between 12 and 18 (S °/₀₀ 22 - 33) and final pH values between 3.0 and 3.9 the total alkalinity may be read directly from Table IV without incurring appreciable errors.

Note 2. If the final pH is greater than 4.0 remove the electrodes, but do not wash them, and pipette 5.00 ml. of 0.01000 N acid into the bottle. Mix the solution and again measure the pH. Calculate a_H and f as

above and substitute in the equation:

$$\text{Total alkalinity} = 3.000 - 1300\left(\frac{a_H}{I}\right)$$

This procedure will be necessary with most ocean waters of S °/₀₀ greater than 33 °/₀₀.

PART II. CALCULATIONS AND USE OF TABLES

Note.

Mg. carbon = millimoles carbon dioxide (in any form) x 12.

1. Calculation of the Carbonate Alkalinity

Required: Total alkalinity (may be obtained from the specific alkalinity and the chlorinity for approximate work), chlorinity or salinity, initial temperature, pH and the temperature at which the pH was measured.

a. Calculate the initial pH of the water from Table IA.

b. Look up the quantity, A milliequivalents per liter, from Table V.

c. Carbonate alkalinity = total alkalinity - A. (milliequivalents/l).

2. Calculation of the Total Carbon Dioxide Content (All Forms)

Required: Total alkalinity (may be obtained from the specific alkalinity and the chlorinity for approximate work), chlorinity or salinity, initial temperature, pH and the temperature at which the pH was measured.

a. Calculate the initial pH of the water from Table IA.

b. Calculate the carbonate alkalinity as in 1. above.

c. Look up the factor F_T in Table VI.

d. Total carbon dioxide content = carbonate alkalinity x F_T (millimoles/l).

3. Calculation of the Partial Pressure and Concentration of Carbon Dioxide

Note: In the equilibrium:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

for sea water only one per cent or less of the total carbon dioxide is in the form of carbonic acid. This equilibrium is attained relatively slowly in sea water. In living tissue

the enzyme carbonic anhydrase greatly accelerates the combination of water and carbon dioxide gas.

Required: Carbonate alkalinity (see 1. above), chlorinity or salinity, initial temperature, pH and the temperature at which the pH was measured.

a. Calculate the initial pH of the water from Table IA.

b. Look up the factor F_p in Table VII.

c. Partial pressure of carbon dioxide, P_{CO_2}, =

$$\text{carbonate alkalinity} \times F_p \text{ (atmospheres)}.$$

d. Look up the solubility of carbon dioxide in unbuffered sea water of a given salinity and temperature from Table VIII. If α is this value in millimoles per liter.

e. Concentration of dissolved carbon dioxide = $P_{CO_2} \times \alpha$ (millimoles/l).

4. Calculation of the Bicarbonate Ion Concentration $[HCO_3^{1-}]$

Required: Carbonate alkalinity (see 1. above), chlorinity or salinity, initial temperature, pH and the temperature at which the pH was measured, the dissociation constant K, where K is defined as:

$$\frac{a_H \times [HCO_3^{1-}]}{P_{CO_2} \times \alpha \times a_{H_2O}}$$

where a_H is measured by a glass electrode and a_{H_2O} is the activity of the water molecules in sea water. Values for K as a function of temperature (in situ) and chlorinity (or salinity) are collected in Table IX.

a. Calculate the initial pH of the water from Table IA.

b. Look up the corresponding a_H value from Table II.

c. Bicarbonate concentration $\left[HCO_3^{1-}\right]$ =

$$\text{carbonate alkalinity} \times \left(\frac{a_H}{a_H + 2K}\right) \text{ as millimoles/l.}$$

5. Calculation of the Carbonate Ion Concentration $\left[CO_3^{2-}\right]$

Required: Carbonate alkalinity (see 1. above), chlorinity or salinity, initial temperature, pH and the temperature at which the pH was measured, the dissociation constant K.

a. Calculate the initial pH of the water from Table IA.

b. Look up the corresponding a_H value from Table II.

c. Carbonate concentration, $\left[CO_3^{2-}\right]$ =

$$\text{carbonate alkalinity} \times \left(\frac{K}{a_H + 2K}\right) \text{as millimoles/l.}$$

Note. If the pH exceeds 8.1:

$$\text{Carbonate concentration, } \left[CO_3^{2-}\right] = \text{total carbon dioxide content} - \left[HCO_3^{1-}\right],$$

where the total carbon dioxide is evaluated as in item II, 2. above.

Approved December 1957 Standard Method C. 1.A

Addendum No. 1

DETERMINATION OF CARBONATE, BICARBONATE AND FREE CARBON DIOXIDE IN SEA WATER FROM PH AND ALKALINITY MEASUREMENTS

Introductory Remarks

Re-determination of the dissociation constants of boric acid and carbonic acid in sea water by Dr. J. Lyman (J. Lyman Ph.D. thesis, U.C.L.A. 1957. Buffer Mechanism of Sea Water) has substantiated the Buch values (K. Buch, Das Kohlensäure gleichgewichtssystem im Meerwasser. Havsforskn Inst. Skr. Helsingf. No. 151. 1951) used to compute the Tables in Standard Method C. 1.A, except for the second dissociation constant of carbonic acid. pK values for this dissociation are now considered to be some 0.15 units higher than previously supposed. The data in Tables VI, VII and IX are consequently subject to revision.

The constant K defined on page 108 of Standard Method C. 1.A and reported in Table IX should be defined as:

$$K = \frac{a_H \times \langle CO_3^{2-} \rangle}{\langle HCO_3^{1-} \rangle}$$

Tables VI, VII and IX are to be deleted and replaced by the following Tables.

PART III. TABLES

Table IA.

Temperature correction for pH values in sea water

If pH_s is the original value of the pH of the sample, in situ, at a temperature t° C and pH_m is the pH measured in the laboratory at t_m° C (generally greater than t° C) then:

$$pH_s = pH_m - x(t - t_m)$$

and x is given in the table.

pH_m	S °/₀₀ = 18 Cl °/₀₀ = 10			S °/₀₀ = 27 Cl °/₀₀ = 15		
	t° C 0-10°	t° C 10-20°	t° C 20-30°	t° C 0-10°	t° C 10-20°	t° C 20-30°
7.4	0.0087	0.0084	0.0069	0.0088	0.0087	0.0076
7.6	0.0092	0.0092	0.0079	0.0095	0.0096	0.0083
7.8	0.0100	0.0101	0.0089	0.0103	0.0105	0.0090
8.0	0.0108	0.0109	0.0094	0.0110	0.0112	0.0094
8.2	0.0114	0.0115	0.0098	0.0115	0.0117	0.0096
8.4	0.0117	0.0117	0.0099	0.0118	0.0118	0.0098
pH_m	S °/₀₀ = 35 Cl °/₀₀ = 19.5			S °/₀₀ = 38 Cl °/₀₀ = 21		
	t° C 0-10°	t° C 10-20°	t° C 20-30°	t° C 0-10°	t° C 10-20°	t° C 20-30°
7.4	0.0089	0.0087	0.0081	0.0092	0.0089	0.0079
7.6	0.0095	0.0095	0.0091	0.0097	0.0098	0.0088
7.8	0.0104	0.0104	0.0098	0.0106	0.0108	0.0093
8.0	0.0110	0.0109	0.0102	0.0112	0.0114	0.0096
8.2	0.0114	0.0112	0.0103	0.0116	0.0116	0.0098
8.4	0.0116	0.0114	0.0104	0.0118	0.0119	0.0100

Table IB.

Pressure correction for pH values in sea water

If pH_d is the original value of the pH of the sample, in situ, at a depth d meters and pH_s is the pH measured under atmospheric pressure, then:

$$pH_d = pH_s - y.d$$

and y is given in the table.

pH_s	$y \times 10^6$	pH_s	$y \times 10^6$
7.5	35	7.9	23
7.6	31	8.0	22
7.7	28	8.1	21
7.8	25	8.2	20
		8.3	20

Table II

Conversion of pH to a_H values from the relation $a_H = 10^{-pH}$.

For a pH of Q + v (where v is the decimal part)

$a_H = N \times 10^{-Q}$, values of v and N being as follows:

v	N	v	N	v	N
0.00	1.000	0.34	0.457	0.67	0.214
0.01	0.977	0.35	0.447	0.68	0.209
0.02	0.955	0.36	0.437	0.69	0.204
0.03	0.933	0.37	0.427	0.70	0.200
0.04	0.912	0.38	0.417	0.71	0.195
0.05	0.891	0.39	0.407	0.72	0.191
0.06	0.871	0.40	0.398	0.73	0.186
0.07	0.851	0.41	0.389	0.74	0.182
0.08	0.832	0.42	0.380	0.75	0.178
0.09	0.813	0.43	0.372	0.76	0.174
0.10	0.794	0.44	0.363	0.77	0.170
0.11	0.776	0.45	0.355	0.78	0.166
0.12	0.759	0.46	0.347	0.79	0.162
0.13	0.741	0.47	0.339	0.80	0.158
0.14	0.725	0.48	0.331	0.81	0.155
0.15	0.709	0.49	0.324	0.82	0.151
0.16	0.692	0.50	0.316	0.83	0.148
0.17	0.676	0.51	0.309	0.84	0.144
0.18	0.661	0.52	0.302	0.85	0.141
0.19	0.646	0.53	0.295	0.86	0.138
0.20	0.631	0.54	0.288	0.87	0.135
0.21	0.617	0.55	0.282	0.88	0.132
0.22	0.603	0.56	0.275	0.89	0.129
0.23	0.589	0.57	0.269	0.90	0.126
0.24	0.575	0.58	0.263	0.91	0.123
0.25	0.562	0.59	0.257	0.92	0.120
0.26	0.549	0.60	0.251	0.93	0.117
0.27	0.537	0.61	0.245	0.94	0.115
0.28	0.525	0.62	0.240	0.95	0.112
0.29	0.513	0.63	0.234	0.96	0.110
0.30	0.501	0.64	0.229	0.97	0.107
0.31	0.490	0.65	0.224	0.98	0.105
0.32	0.479	0.66	0.219	0.99	0.102
0.33	0.468				

Table III.

Factor f in equation:

$$\text{Total alkalinity} = 2.500 - 1250\left(\frac{a_H}{f}\right)$$

as a function of chlorinity or salinity.

pH Range	Cl °/₀₀ S °/₀₀	2 3.5	4 7	6 11	8 14.5	10 18	12-18 21-33	20 36
2.8-2.9	f	0.865	0.800	0.785	0.775	0.770	0.768	0.773
3.0-3.9	f	0.845	0.782	0.770	0.760	0.755	0.753	0.758
3.9-4.0	f	0.890	0.822	0.810	0.800	0.795	0.793	0.798

Table IV

Total alkalinity (1 liter 20° C) as a function of the final pH of the solution obtained from 100.0 ml. of sample and 25.00 ml. of 0.01000 N hydrochloric acid. This table may be used for samples of chlorinity between 12 °/₀₀ and 18 °/₀₀, or salinities between 21 °/₀₀ and 33 °/₀₀.

pH	Total Alkalinity	pH	Total Alkalinity	pH	Total Alkalinity
3.00	0.84	3.30	1.67	3.60	2.08
3.02	0.92	3.32	1.71	3.62	2.10
3.04	0.99	3.34	1.74	3.64	2.12
3.06	1.06	3.36	1.77	3.66	2.14
3.08	1.12	3.38	1.81	3.68	2.15
3.10	1.19	3.40	1.84	3.70	2.17
3.12	1.24	3.42	1.87	3.72	2.18
3.14	1.30	3.44	1.90	3.74	2.20
3.16	1.35	3.46	1.93	3.76	2.21
3.18	1.40	3.48	1.95	3.78	2.23
3.20	1.45	3.50	1.98	3.80	2.24
3.22	1.50	3.52	2.00	3.82	2.25
3.24	1.55	3.54	2.02	3.84	2.26
3.26	1.59	3.56	2.04	3.86	2.27
3.28	1.63	3.58	2.06	3.88	2.28
				3.90	2.29

Table V

Quantity, A, milliequivalents per liter, to be subtracted from the total alkalinity to give the carbonate alkalinity in milliequivalents per liter.

Note. Multiply the figure in the table by 10^{-2} to get A.

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl °/₀₀ = 15 S °/₀₀ = 27															
7.3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
7.4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
7.5	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2
7.6	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2
7.7	2	2	2	2	2	2	2	2	2	2	2	3	3	3	3	3
7.8	2	2	2	2	2	3	3	3	3	3	3	3	3	3	3	4
7.9	3	3	3	3	3	3	3	3	4	4	4	4	4	4	4	4
8.0	3	3	4	4	4	4	4	4	4	5	5	5	5	5	5	5
8.1	4	4	4	4	5	5	5	5	5	5	6	6	6	6	6	6
8.2	5	5	5	5	6	6	6	6	6	7	7	7	7	7	8	8
8.3	6	6	6	7	7	7	7	7	8	8	8	8	9	9	9	9
8.4	7	7	8	8	8	8	9	9	9	9	10	10	10	10	11	11
8.5	8	9	9	9	10	10	10	10	11	11	11	11	12	12	12	13
8.6	10	10	11	11	11	12	12	12	12	13	13	13	14	14	14	14
8.7	12	12	12	13	13	13	14	14	14	14	15	15	16	16	16	16
8.8	15	15	15	15	16	16	17	17	17	17	18	18	18	19	19	19
	Cl °/₀₀ = 17 S °/₀₀ = 31															
7.3	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1
7.4	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2
7.5	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2
7.6	2	2	2	2	2	2	2	2	2	2	2	3	3	3	3	3
7.7	2	2	2	2	2	3	3	3	3	3	3	3	3	3	3	4
7.8	3	3	3	3	3	3	3	3	4	4	4	4	4	4	4	4
7.9	3	3	3	4	4	4	4	4	4	4	5	5	5	5	5	5
8.0	4	4	4	4	5	5	5	5	5	5	6	6	6	6	6	6
8.1	5	5	5	5	6	6	6	6	6	7	7	7	7	8	8	8
8.2	6	6	6	6	7	7	7	7	8	8	8	8	9	9	9	9
8.3	7	7	8	8	8	8	9	9	9	9	10	10	10	11	11	11
8.4	8	9	9	9	10	10	10	11	11	11	11	12	12	12	13	13
8.5	10	10	11	11	11	12	12	12	13	13	13	14	14	14	15	15
8.6	12	12	13	13	13	14	14	14	15	15	15	16	16	16	17	17
8.7	14	14	15	15	16	16	16	16	17	17	18	18	18	19	19	19
8.8	17	17	18	18	19	19	19	20	20	20	21	21	21	22	22	23

Table V (cont'd)

Quantity, A, milliequivalents per liter, to be subtracted from the total alkalinity to give the carbonate alkalinity in milliequivalents per liter.

Note. Multiply the figure in the table by 10^{-2} to get A.

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl °/₀₀ = 19 S °/₀₀ = 34															
7.3	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1
7.4	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2
7.5	2	2	2	2	2	2	2	2	2	2	2	2	3	3	3	3
7.6	2	2	2	2	2	2	3	3	3	3	3	3	3	3	3	3
7.7	2	3	3	3	3	3	3	3	3	3	4	4	4	4	4	4
7.8	3	3	3	3	4	4	4	4	4	4	4	5	5	5	5	5
7.9	4	4	4	4	4	5	5	5	5	5	5	6	6	6	6	6
8.0	5	5	5	5	5	6	6	6	6	6	7	7	7	7	7	8
8.1	6	6	6	6	7	7	7	7	8	8	8	8	8	9	9	9
8.2	7	7	7	8	8	8	9	9	9	9	10	10	10	10	11	11
8.3	8	9	9	9	10	10	10	10	11	11	11	12	12	12	13	13
8.4	10	10	11	11	11	12	12	12	13	13	13	14	14	14	15	15
8.5	12	12	13	13	13	14	14	14	15	15	16	16	16	17	17	17
8.6	14	14	15	15	16	16	16	17	17	18	18	18	19	19	19	20
8.7	16	16	17	17	18	18	19	19	19	20	20	20	21	21	22	22
8.8	19	20	20	21	21	22	22	22	23	23	24	24	24	25	25	25
	Cl °/₀₀ = 21 S °/₀₀ = 38															
7.3	0	1	1	1	1	1	1	1	1	1	1	1	1	1	2	2
7.4	1	2	2	2	2	2	2	2	2	2	2	2	2	2	3	3
7.5	2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	3
7.6	2	2	2	3	3	3	3	3	3	3	3	4	4	4	4	4
7.7	3	3	3	3	3	4	4	4	4	4	4	4	4	5	5	5
7.8	4	4	4	4	4	4	5	5	5	5	5	5	6	6	6	6
7.9	4	4	5	5	5	5	6	6	6	6	6	7	7	7	7	7
8.0	5	6	6	6	6	7	7	7	7	7	8	8	8	8	9	9
8.1	7	7	7	7	8	8	8	8	9	9	9	10	10	10	10	11
8.2	8	8	9	9	9	10	10	10	10	11	11	11	12	12	12	13
8.3	10	10	10	11	11	11	12	12	12	13	13	14	14	14	15	15
8.4	11	11	11	12	12	13	13	13	14	14	14	15	15	15	16	16
8.5	14	14	14	15	15	16	16	17	17	17	18	18	19	19	20	20
8.6	16	16	17	17	18	18	19	19	20	20	21	21	22	22	22	23
8.7	18	19	19	20	20	21	21	22	22	23	23	24	24	24	25	25
8.8	22	22	23	23	24	24	25	25	26	26	27	27	28	28	28	29

Table VI

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 15 ‰								S = 27 ‰							
7.3	1.07	1.06	1.06	1.06	1.05	1.05	1.05	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03
7.4	1.05	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02
7.5	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00
7.6	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	.99	.99
7.7	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98
7.8	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97
7.9	.99	.99	.99	.99	.98	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96
8.0	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94
8.1	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.93	.93	.93
8.2	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91	.91
8.3	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91	.91	.90	.90	.89	.89
8.4	.93	.93	.93	.92	.92	.92	.91	.91	.90	.90	.89	.89	.88	.88	.87	.86
8.5	.92	.91	.91	.91	.90	.90	.89	.89	.88	.88	.87	.86	.86	.85	.85	.84
8.6	.90	.89	.89	.89	.88	.88	.87	.87	.86	.85	.85	.84	.83	.83	.82	.81

Table VI (cont'd)

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 17 ‰								S = 30.5 ‰							
7.3	1.06	1.06	1.06	1.05	1.05	1.05	1.04	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03
7.4	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.02	1.01
7.5	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.00	1.00
7.6	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99
7.7	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.98	.98	.98	.98
7.8	1.00	1.00	1.00	.99	.99	.99	.99	.98	.98	.98	.98	.98	.97	.97	.97	.96
7.9	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.95	.95
8.0	.98	.98	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94
8.1	.97	.97	.96	.96	.96	.95	.95	.95	.95	.94	.94	.94	.93	.93	.92	.92
8.2	.96	.95	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.92	.91	.91	.90
8.3	.94	.94	.94	.93	.93	.92	.92	.92	.91	.91	.90	.90	.90	.89	.88	.88
8.4	.93	.92	.92	.92	.91	.91	.90	.90	.89	.89	.88	.88	.87	.87	.86	.86
8.5	.91	.91	.90	.90	.89	.89	.88	.88	.87	.87	.86	.86	.85	.84	.84	.83
8.6	.89	.89	.88	.87	.87	.86	.86	.85	.85	.84	.84	.83	.82	.82	.81	.80

Table VI (cont'd)

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C / $pH_{S.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 19 ‰							S = 34 ‰								
7.3	1.06	1.06	1.05	1.05	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02
7.4	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01
7.5	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00
7.6	1.02	1.02	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.98
7.7	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97
7.8	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96
7.9	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.94
8.0	.98	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93
8.1	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91
8.2	.95	.95	.95	.94	.94	.94	.93	.93	.92	.92	.92	.91	.91	.90	.90	.89
8.3	.94	.93	.93	.93	.92	.92	.91	.91	.91	.90	.90	.89	.89	.88	.88	.87
8.4	.92	.92	.91	.91	.90	.90	.90	.89	.89	.88	.88	.87	.86	.86	.85	.84
8.5	.90	.90	.89	.89	.88	.88	.87	.87	.86	.86	.85	.85	.84	.83	.83	.82
8.6	.88	.88	.87	.87	.86	.86	.85	.84	.84	.83	.83	.82	.81	.81	.80	.79

Table VI (cont'd)

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C / $pH_{S.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 21 ‰								S = 38 ‰							
7.3	1.06	1.05	1.05	1.04	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02
7.4	1.04	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.00
7.5	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99
7.6	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98
7.7	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97
7.8	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.95
7.9	.98	.98	.98	.97	.97	.97	.97	.97	.96	.96	.96	.95	.95	.95	.94	.94
8.0	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93	.92
8.1	.96	.96	.95	.95	.95	.95	.94	.94	.93	.93	.93	.92	.92	.91	.91	.90
8.2	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91	.91	.90	.90	.89	.89	.88
8.3	.93	.93	.92	.92	.92	.91	.91	.90	.90	.89	.89	.88	.88	.87	.86	.86
8.4	.91	.91	.91	.90	.90	.89	.89	.88	.88	.87	.87	.86	.85	.85	.84	.83
8.5	.89	.89	.89	.88	.88	.87	.86	.86	.85	.85	.84	.84	.83	.82	.81	.80
8.6	.87	.87	.86	.86	.85	.85	.84	.83	.83	.82	.82	.81	.80	.79	.78	.77

Table VII

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 15 ‰								S = 27 ‰							
7.3	1.12	1.14	1.17	1.19	1.22	1.26	1.29	1.32	1.36	1.39	1.42	1.45	1.49	1.54	1.59	1.64
7.4	.89	.90	.92	.94	.97	1.00	1.02	1.05	1.07	1.10	1.12	1.15	1.17	1.21	1.25	1.29
7.5	.70	.71	.73	.74	.77	.79	.81	.83	.85	.87	.88	.90	.93	.96	.99	1.01
7.6	.56	.56	.58	.59	.60	.62	.64	.65	.67	.68	.70	.71	.73	.75	.78	.80
7.7	.44	.44	.45	.46	.48	.49	.50	.51	.53	.54	.55	.56	.57	.59	.61	.62
7.8	.35	.35	.36	.36	.37	.39	.39	.40	.41	.42	.43	.44	.45	.46	.47	.49
7.9	.27	.27	.28	.29	.29	.30	.31	.31	.32	.33	.33	.34	.35	.36	.37	.38
8.0	.21	.21	.22	.22	.23	.24	.24	.25	.25	.26	.26	.26	.27	.28	.29	.29
8.1	.17	.17	.17	.17	.18	.18	.19	.19	.20	.20	.20	.20	.21	.21	.22	.22
8.2	.13	.13	.13	.14	.14	.14	.15	.15	.15	.15	.16	.16	.16	.16	.17	.17
8.3	.10	.10	.10	.10	.11	.11	.11	.11	.12	.12	.12	.12	.12	.12	.13	.13
8.4	.08	.08	.08	.08	.08	.08	.09	.09	.09	.09	.09	.09	.09	.09	.10	.10
8.5	.06	.06	.06	.06	.06	.06	.06	.07	.07	.07	.07	.07	.07	.07	.07	.07
8.6	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VII (cont'd)

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 17 ‰							S = 30.5 ‰								
7.3	1.09	1.10	1.13	1.16	1.19	1.23	1.26	1.29	1.31	1.34	1.37	1.41	1.44	1.49	1.54	1.57
7.4	.86	.87	.89	.91	.94	.97	1.00	1.02	1.04	1.06	1.08	1.11	1.14	1.18	1.22	1.24
7.5	.68	.69	.71	.72	.74	.77	.79	.80	.82	.84	.85	.87	.90	.93	.96	.97
7.6	.54	.54	.56	.57	.59	.60	.62	.63	.64	.66	.67	.69	.70	.73	.75	.76
7.7	.42	.43	.44	.45	.46	.48	.49	.50	.51	.52	.53	.54	.55	.57	.59	.60
7.8	.33	.34	.35	.35	.36	.37	.38	.39	.40	.40	.41	.42	.43	.44	.46	.46
7.9	.26	.26	.27	.28	.28	.29	.30	.31	.31	.32	.32	.33	.34	.35	.36	.36
8.0	.21	.21	.21	.22	.22	.23	.23	.24	.24	.25	.25	.25	.26	.27	.27	.28
8.1	.16	.16	.17	.17	.17	.18	.18	.18	.19	.19	.19	.20	.20	.21	.21	.21
8.2	.12	.13	.13	.13	.13	.14	.14	.14	.14	.15	.15	.15	.15	.16	.16	.16
8.3	.10	.10	.10	.10	.10	.10	.11	.11	.11	.11	.11	.11	.12	.12	.12	.12
8.4	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08	.09	.09	.09	.09	.09	.09
8.5	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.07	.07	.07	.07
8.6	.04	.04	.04	.04	.04	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VII (cont'd)

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 19‰								S = 34 ‰							
7.3	1.05	1.07	1.10	1.12	1.14	1.18	1.21	1.24	1.28	1.30	1.33	1.36	1.40	1.43	1.48	1.52
7.4	.83	.84	.87	.89	.90	.93	.96	.98	1.01	1.02	1.05	1.07	1.10	1.13	1.17	1.20
7.5	.66	.67	.69	.70	.71	.74	.76	.77	.80	.81	.82	.84	.87	.89	.92	.94
7.6	.52	.53	.54	.55	.56	.58	.60	.61	.63	.63	.65	.66	.68	.70	.72	.74
7.7	.41	.41	.43	.44	.44	.46	.47	.48	.49	.50	.51	.52	.53	.54	.56	.58
7.8	.32	.33	.33	.34	.35	.36	.37	.37	.39	.39	.40	.41	.42	.42	.44	.45
7.9	.25	.26	.26	.27	.27	.28	.29	.29	.30	.30	.31	.32	.32	.33	.34	.35
8.0	.20	.20	.20	.21	.21	.22	.22	.23	.23	.23	.24	.24	.25	.25	.26	.27
8.1	.15	.16	.16	.16	.16	.17	.17	.18	.18	.18	.18	.19	.19	.19	.20	.20
8.2	.12	.12	.12	.13	.13	.13	.13	.14	.14	.14	.14	.14	.15	.15	.15	.15
8.3	.09	.09	.10	.10	.10	.10	.10	.10	.11	.11	.11	.11	.11	.11	.11	.12
8.4	.07	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08	.08	.09	.09
8.5	.05	.05	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06
8.6	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.05	.05	.05

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VII (cont'd)

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C / pH s.d.	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 21 ‰								S = 38 ‰							
7.3	1.02	1.04	1.07	1.08	1.11	1.15	1.18	1.20	1.24	1.26	1.29	1.32	1.36	1.39	1.44	1.47
7.4	.81	.82	.84	.85	.88	.91	.94	.95	.98	.99	1.01	1.04	1.07	1.09	1.13	1.15
7.5	.64	.65	.67	.67	.69	.72	.74	.75	.77	.78	.80	.82	.84	.86	.89	.90
7.6	.50	.51	.53	.53	.55	.57	.58	.59	.60	.61	.63	.64	.66	.67	.70	.71
7.7	.40	.40	.41	.42	.43	.44	.46	.46	.47	.48	.49	.50	.51	.53	.54	.55
7.8	.31	.32	.32	.33	.34	.35	.36	.36	.37	.37	.38	.39	.40	.41	.42	.43
7.9	.24	.25	.25	.26	.26	.27	.28	.28	.29	.29	.30	.30	.31	.32	.33	.33
8.0	.19	.19	.20	.20	.20	.21	.22	.22	.22	.23	.23	.23	.24	.24	.25	.25
8.1	.15	.15	.15	.15	.16	.16	.17	.17	.17	.17	.18	.18	.18	.19	.19	.19
8.2	.11	.12	.12	.12	.12	.13	.13	.13	.13	.13	.14	.14	.14	.14	.14	.14
8.3	.09	.09	.09	.09	.09	.10	.10	.10	.10	.10	.10	.10	.10	.11	.11	.11
8.4	.07	.07	.07	.07	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08
8.5	.05	.05	.05	.05	.05	.05	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06
8.6	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VIII

Solubility, (α) millimoles per liter, of carbon dioxide in sea water.

S°/₀₀	°C / Cl°/₀₀	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
27	15	67.4	62.3	57.8	53.8	50.4	47.2	44.2	41.6	39.3	37.1	35.1	33.1	31.4	29.9	28.4	27.0
28	16	66.7	61.7	57.3	53.3	49.9	46.8	43.8	41.3	39.0	36.8	34.8	32.9	31.2	29.7	28.1	26.8
30.5	17	66.0	61.1	56.7	52.8	49.5	46.4	43.4	41.0	38.7	36.5	34.6	32.7	31.0	29.4	27.9	26.6
32.5	18	65.3	60.5	56.2	52.4	49.0	46.0	43.1	40.6	38.4	36.2	34.3	32.4	30.7	29.2	27.7	26.4
34	19	64.6	59.9	55.7	51.9	48.6	45.6	42.8	40.3	38.1	35.9	34.0	32.1	30.4	28.9	27.5	26.2
36	20	64.0	59.3	55.1	51.4	48.2	45.2	42.4	40.0	37.7	35.6	33.7	31.9	30.2	28.7	27.3	26.0
38	21	63.3	58.7	54.6	50.9	47.7	44.8	42.1	39.6	37.4	35.4	33.5	31.7	30.0	28.5	27.1	25.8

Table IX

Values for K, the quasi-thermodynamic second dissociation constant of carbonic acid in sea water.

Note. Multiply the figures in the table by 10^{-9} to get K

S ‰ \ °C / Cl ‰	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
27	15	0.33	0.35	0.36	0.38	0.40	0.42	0.45	0.47	0.50	0.53	0.56	0.60	0.63	0.67	0.72	0.76
28	16	0.35	0.37	0.38	0.41	0.43	0.45	0.47	0.50	0.53	0.56	0.59	0.63	0.66	0.71	0.75	0.79
30.5	17	0.36	0.38	0.40	0.43	0.45	0.48	0.50	0.53	0.55	0.59	0.62	0.65	0.69	0.73	0.78	0.83
32.5	18	0.38	0.40	0.42	0.45	0.47	0.50	0.53	0.55	0.58	0.62	0.65	0.69	0.73	0.77	0.83	0.88
34	19	0.40	0.42	0.44	0.47	0.50	0.52	0.55	0.58	0.61	0.65	0.68	0.72	0.76	0.81	0.86	0.93
36	20	0.42	0.44	0.46	0.49	0.53	0.55	0.58	0.61	0.65	0.68	0.71	0.76	0.80	0.85	0.91	0.98
38	21	0.44	0.47	0.48	0.52	0.54	0.56	0.60	0.63	0.67	0.71	0.74	0.79	0.84	0.90	0.97	1.05

The following pages contain lists

of the chemicals and equipment required for the

methods described in this volume.

STANDARD METHOD NO. SAL. 3.A

Title: Determination of Salinity by Conductivity Measurement

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

None.

B. Chemicals per sample analysed

None.

C. Other Chemicals

1. Eau de Mer Normale (Copenhagen water) 3 bottles per 20 liter carboy of secondary standard that is used.

2. Secondary Standard water: Allow about 1500 ml. per working day.

3. Distilled water. A very modest amount is required for filling cells prior to shut down periods. Two to three liters should suffice.

4. Paraffin oil. One or two hundred ml. should be aboard to cover the surface of substandard samples.

5. Thymol. A few grams of thymol from which to take a few crystals for the stabilization of each new batch of secondary standard sea water.

EQUIPMENT REQUIRED

A. Basic Equipment

1. Salinometer and kit.
2. Two jigger dispensing units.
3. Tube and clip for dispensing water from Copenhagen water samples.
4. Spare copies of salinity tables.
5. Large funnel and 18 cm. No.1 Whatman Filter papers for filtering secondary standard sea water into carboy.

B. Equipment for the analysis of a batch of samples

1. Up to 25 flat 8 oz. medicinal bottles that have had several years previous history of salinity sample storage.
2. Sufficient waxed corks for above bottles.
3. Labels for above bottles.
   Note. If samples are analysed directly they are taken then a total of some 50 bottles and corks should be sufficient but, in case of a salinometer breakdown, sufficient bottles, corks and wax should be on board to allow all samples to be stored as described in the method.

STANDARD METHOD NO. O. 1.A

Title: Determination of Oxygen in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

1. 0.01 N thiosulphate n x 30 ml. Add to requirement in B. 5.
2. 0.0100 N biiodate n x 35 ml.
3. Starch indicator solution n x 2.5 ml. Add to requirement B. 4.

B. Chemicals per sample analysed

1. Manganous sulphate (Reagent No. 1) n x 1.1 ml.
2. Alkaline iodide solution (Reagent No. 2) n x 1.1 ml.
3. Concentrated H_2SO_4 (Reagent No. 3) n x 1.2 ml.
4. Starch indicator solution n x 2.5 ml.
5. 0.01 N $Na_2S_2O_3$ n x 13 ml.

C. Other chemicals

None

No. O. 1.A

EQUIPMENT REQUIRED

A. Basic Equipment

1. One clean automatic 25 ml. burette and spare = 2 x 25 ml. automatic burette.

2. One clean 10 ml. pipette and spare = 2 x 10 ml. pipettes.

3. One clean 100 ml. pipette and spare = 2 x 100 ml. pipettes.

4. 3 x 2 ml. automatic bulb pipettes set at 1.0 ± 0.1 ml. for dispensing Reagents Nos. 1, 2 and 3 and 2 spare pipettes = 5 x 2 ml. automatic bulb pipettes.

5. One Winchester quart bottle for temporary storage of thiosulphate solution.

6. 1 x 250 ml. capacity bottle for temporary storage of starch indicator.

7. 3 x 8 oz. medicine bottles for temporary storage of Reagents Nos. 1, 2 and 3.

B. Equipment for the analysis of a batch of samples

1. Up to 25 x 300 ml. numbered B.O.D. bottles with stoppers of matching number.

STANDARD METHOD NO. P. 1.A AND ADDENDUM NO. 1

Title: Determination of Inorganic Phosphorus (Phosphate) in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

1. Synthetic Sea water n x 550 ml. for standards and blanks.
2. Standard Phosphate (concn) n x 1.0 ml. (Minimum of 35 ml.)
3. Stannous chloride stock solution n x 13 ml. (Minimum of 100 ml.)
4. 5 per cent hydrochloric acid in boiled out water n x 50 ml. (Minimum of 500 ml.)

B. Chemicals per sample analysed

1. Molybdate Reagent (Reagent No. 1) n x 1.1 ml.

C. Other Chemicals

1. 25 ml. of good quality chloroform for stabilizing dilute standard solutions.
2. Distilled water. There is a moderate requirement for distilled water for use in the determination of Reagent blanks and the rinsing of glassware. About 2 liters should be taken for each cruise.

EQUIPMENT REQUIRED

A. Basic Equipment

1. Beckman DU Spectrophotometer and kit (10 cm. cells required).

2. One clean 50 ml. burette and spare for measuring out standard = 2 x 50 ml. burettes.

3. One clean 10 ml. pipette and spare for diluting standard and stannous chloride = 2 x 10 ml. pipettes.

4. 2 x 2 ml. automatic bulb pipettes, one set at 1.0 ± 0.1 ml. and the other at 0.5 ± 0.05 ml., for dispensing Reagents Nos. 1 and 2, and 2 spare pipettes = 4 x 2 ml. automatic bulb pipettes.

5. 1 liter volumetric flask for diluting standard.

6. 1 50 ml. graduated cylinder and spare for diluting stannous chloride = 2 x 50 ml. graduated cylinders.

7. One 100 ml. stoppered graduated measuring cylinder and spare for preparing standards and blanks = 2 x 100 ml. stoppered graduated measuring cylinders.

8. 1 x 100 ml. glass bottle for temporary storage of dilute stannous chloride solution.
   1 x 500 ml. polyethylene bottle for temporary storage of molybdate Reagent.
   2 x 500 ml. dark glass bottle for storage of dilute standard.

9. One small polyethylene funnel and 1 x 250 ml polyethylene beaker for general convenience in preparing solutions, etc.

10. A thermostatically controlled water bath set at 23° C ± 1° C.

B. Equipment for the analysis of a batch of samples

Up to 30 x 130 ml. screw-top polyethylene bottles marked at 100 ml. by black tape.

STANDARD METHOD NO. P. 2.A. AND ADDENDUM NO. 1

Title: Determination of Total Phosphorus in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

None

B. Chemicals per sample analysed

1. Concentrated hydrochloric acid. n x 0.1 ml.

C. Other Chemicals

None

EQUIPMENT REQUIRED

A. Basic Equipment

1. 1 x 50 ml. pipette and spare for dispensing sample = 2 x 50 ml. pipettes.

2. Cases for storing tubes containing samples.

B. Equipment for the analysis of a batch of samples

None

C. Extra Equipment per sample analysed

One 80 ml. Pyrex test tube per sample to be returned to shore base laboratory. The tubes, containing acidified water, are prepared as described in Standard Method No. P. 2.A, Addendum No. 1.

STANDARD METHOD NO. P. 3.A

Title: Determination of Total Particulate Phosphorus in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

None

B. Chemicals per sample analysed

1. Concentrated hydrochloric acid n x 0.1 ml.

2. Distilled water. There is a relatively heavy demand for distilled water for rinsing and washing filters, etc. Allow about 200 ml. a sample.

EQUIPMENT REQUIRED

A. Basic Equipment

1. 1 x 250 plus 1 x 500, plus 1 x 1000 ml. clean measuring cylinders for measuring out the initial samples (according to anticipated particulate phosphorus content).

2. Cases for storing flasks containing the samples.

3. Parafilm sheeting to cover the mouth of flasks for storage.

4. One or two (according to the number of samples and the pressure of other work) Pyrex Millipore filter holders each with clamp. Similarly 1 or 2 liter glass Buckner flasks to contain filtrates, which may be reserved for other phosphorus determinations (ref. Standard Method No. P. 4.A).

B. Equipment for the analysis of a batch of samples

None.

C. Extra equipment per sample analysed

One HA 0.047 mm. plain white Millipore filter membrane and one special 125 ml. Pyrex Erlenmeyer flask per sample.
For conditioning of the flask, etc., see Standard Method No. P. 4.A).

STANDARD METHOD NO. SI. 1.A

Title: Determination of Soluble Silicate in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

1. Metol sulphite Solution — n x 125 ml.
2. Oxalic acid Solution — n x 75 ml.
3. 50 per cent sulphuric acid — n x 75 ml.
4. Distilled water for reagent blanks is only required in quantity if many measurements are made using 10 cm. cells. The water must be stored in polyethylene and 100 ml. allowed per batch of samples.

B. Chemicals per sample analysed

1. Molybdate Reagent (Reagent No. 1) — n x 13 ml.

C. Other Chemicals

To check the method in an emergency each cruise should carry 250 ml. of dilute silicate standard in standard sea water. A few hundred ml. of standard sea water should be available for blank determinations.

EQUIPMENT REQUIRED

A. Basic Equipment

1. Beckman DU Spectrophotometer and kit (1 cm. cells and occasionally 10 cm. cells are required).
2. One 300 ml. polyethylene wash bottle to contain molybdate reagent and one for reducing reagent = 2 x 300 ml. polyethylene wash bottles.
3. 1 x 25 ml. pipette for samples and spare = 2 x 25 ml. pipettes.
4. One medium size polyethylene funnel and 1 x 500 ml. polyethylene beaker for preparing solutions, etc.

B. Equipment for the analysis of a batch of samples

1. Up to 25 x 50 ml. polyethylene bottles for temporary storage of samples prior to analysis.
2. Up to 25 x 50 ml. stoppered graduated glass measuring cylinders cleaned before each cruise by soaking in cleaning mixture.

STANDARD METHOD NO. N. 1.A

Title: Determination of Nitrite in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

1. Sulphanilamide Solution (Reagent No. 1) n x 2 ml. Add to requirement in B.1.

2. N-napthylethylenediamine Solution (Reagent No. 2) n x 2 ml. Add to requirement in B.

3. Distilled water. n x 130 ml.

B. Chemicals per sample analysed

1. Sulphanilamide Solution (Reagent No. 1) n x 1.1 ml.

2. N-napthylethylenediamine Solution (Reagent No. 2) n x 1.1 ml.

C. Other Chemicals

To check the method in an emergency each cruise should carry about 50 ml. of concentrated nitrite standard. A 10 ml. pipette and 1000 ml. flask are required for the dilution of this standard but are probably available if Method P. 1.A is carried out on the same cruise.

EQUIPMENT REQUIRED

A. Basic Equipment

1. Beckman DU Spectrophotometer and kit (10 cm. cells required).
2. 1 x 2.00 ml. graduated pipette in case standard nitrite solution is dispensed.
3. 2 x 2 ml. automatic bulb pipettes, both set at 1.0 ± 0.1 ml., for dispensing Reagents Nos. 1 and 2, and 2 spare pipettes = 4 x 2 ml. automatic bulb pipettes.
4. 1 x 50 ml. measuring cylinder and spare for initial measurement of sample volume = 2 x 50 ml. measuring cylinders.
5. 1 x 250 ml. polyethylene bottle for temporary storage of Reagent No. 1.
6. 1 x 250 ml. glass bottle, dark, for temporary storage of Reagent No. 2.
7. One small polyethylene funnel for transferring solutions.

B. Equipment for the analysis of a batch of samples

1. Up to 25 x 125 ml. Pyrex Erlenmeyer flasks.

STANDARD METHOD NO. N. 2.A

Title: Determination of Nitrate in Sea Water

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

1. Phenol Solution n x 30 ml.
2. Sodium hydroxide Solution n x 30 ml.
3. Copper Sulphate Solution n x 6 ml.
4. Hydrazine Sulphate Solution n x 30 ml.
5. A little re-distilled water is needed for blank determinations. The demand depends on the number of low nitrate determinations to be made. Generally 500 ml. is sufficient on a cruise and should be reserved exclusively for nitrate.
6. Synthetic Sea water for Nitrate n x 250 ml.
(This assumes calibration with each batch of samples and is a very safe maximum, normally only 1 to 2 liters should suffice.)
7. Concentrated standard nitrate solution n x 2 ml.
(Minimum of 60 ml.).

B. Chemicals per sample analysed

1. Acetone (Reagent No. 3) n x 3 ml.
2. Sulphanilamide Solution (Reagent No. 4) n x 1.1 ml.
3. napthylethylenediamine Solution (Reagent No.5) n x 1.1 ml.

C. Other Chemicals

1. There is a moderate requirement for ordinary distilled water for rinsing apparatus and for diluting the reducing reagent (Reagent No. 2). Allow about 5 liters a cruise.

EQUIPMENT REQUIRED

A. Basic Equipment

1. Beckman DU Spectrophotometer and kit (1 cm. cells or 10 cm. cells may be required).

2. Thermostatically controlled water bath set at 23° C.

3. Covered wooden box or partitioned cupboard space for storing up to 30 x 125 ml. Erlenmeyer flasks out of the light.

4. One or more filter stands holding a total of at least 12 funnels.

5. Automatic suction device for use with 25 ml. pipettes.

6. 2 x 100 ml. glass beakers and spare for holding buffer and reductant = 3 x 100 ml. beakers.

7. One 50 ml. measuring cylinder and spare for measuring final sample volume = 2 x 50 ml. measuring cylinders.

8. 1 x 50 ml. volumetric flask and spare for making reductant = 2 x 50 ml. measuring flasks.

9. 1 x 250 ml. polyethylene bottle for temporary storage of Reagent No. 4.

10. 1 x 1000 ml. volumetric flask for preparing dilute nitrate standard.

11. 1 x 2 ml. automatic bulb pipette set for 2.00 ml. $\pm$ 0.25 ml.
plus 1 x 2 ml. automatic bulb pipette set for 2 ml. $\pm$ 0.2 ml.
plus 1 x 2 ml. automatic bulb pipette set for 1.00 ml $\pm$ 0.05 ml.
plus 2 x 2 ml. automatic bulb pipettes each set for 1.0 ml. $\pm$ 0.1 ml.
3 spares should be carried = 8 x 2 ml. automatic bulb pipettes
(Note two of these plus 2 spares will be aboard if Method No. N. 1.A is being used and only 4 extra pipettes need then be taken.)

12. 1 x 5 ml. pipette and spare for copper solution = 2 x 5 ml. pipettes.

13. 3 x 25 ml. pipettes (for measuring phenol, sodium hydroxide and hydrazine) and 1 spare = 4 x 25 ml. pipettes.

14. 1 x 500 ml. polyethylene bottle for temporary storage of sodium hydroxide solution.

A. Basic Equipment (Con'td)

15. 1 x 500 ml. dark glass bottle for temporary storage of phenol solution.

16. 1 x 500 ml. dark glass bottle for temporary storage of hydrazine solution.

17. 1 x 250 ml. dark glass bottle for temporary storage of Reagent No. 5.

18. One small polyethylene funnel for transferring solutions.

19. 2 x 500 ml. dark glass bottle for dilute nitrate standard.

20. 1 x 100 ml. glass bottle for temporary storage of acetone.

B. Equipment for the analysis of a batch of samples

1. Up to 25 polyethylene filter funnels but it is probably satisfactory to filter in two or more batches of 5 to 10 samples a time, cutting the requirement to 10 to 12 funnels.

2. Up to 25 x 100 ml. glass beakers for temporary storage of filtrates.

3. Up to 50 x 125 ml. Erlenmeyer flasks specially pre-treated, (so that two batches can be used at once.) (See Method No. N. 2.A).

C. Equipment required per sample analysed

1. 12.5 cm. diameter No. 42 Whatman filter papers n x 0.01 boxes of 100 circles.

STANDARD METHOD NO. C. 1.A

Title: Determination of Carbonate, Bicarbonate and Free Carbon Dioxide in Sea Water.

CHEMICALS REQUIRED

A. Chemicals per batch of samples analysed

1. Concentrated buffer solution pH 6.87 n x 4 ml. (Minimum of 125 ml.).
2. Buffer solution pH 4.00 n x 25 ml. (Minimum of 500 ml.).

B. Chemicals per sample analysed

1. Standard hydrochloric acid 1.00 N. n x 0.35 (Minimum of 25 ml.). (0.0100 N prepared by diluting 10.0 ml. to 1000 ml.).

C. Other Chemicals

1. There is a moderate requirement for distilled water for electrode washing and storage, etc. 3 liters per cruise.

EQUIPMENT REQUIRED

A. Basic Equipment

1. Beckman Model G pH meter and kit.

2. Thermostatically controlled water bath set in the range 20 to 25° C to ± 1° C.

3. 1 x 1000 ml. volumetric flask for diluting phosphate (pH 6.87) buffer.

4. 1 x 1000 ml. volumetric flask used in the dilution of 1.00 to 0.0100 N acid.

5. One liter screw-cap polyethylene bottle for holding dilute pH 6.87 buffer and 1 liter screw-cap polyethylene bottle for temporary storage of dilute pH 4.00 buffer = 2 x 1000 liter polyethylene bottles.

6. 1 x 5 ml. pipette and spare for adding extra standard acid = 2 x 5 ml. pipettes.

7. 1 x 10 ml. pipette and spare for use in diluting 1.00 to 0.0100 N acid = 2 x 10 ml. pipettes.

8. 1 x 25 ml. pipette and spare for adding standard acid = 2 x 25 ml. pipettes.

9. 1 x 100 ml. pipette and spare for taking alkalinity water sample = 2 x 100 ml. pipettes.

10. Polyethylene wash bottle containing distilled water.

11. 1 x 250 ml. polyethylene beaker for soaking glass electrode, etc., when not in use.

12. One 0 - 35° C thermometer graduated in 0.2° C to check temperature of samples.

B. Equipment for the analysis of a batch of samples

1. Up to 25 x 50 ml. wide-mouth screw-cap polyethylene bottles for pH measurements.

2. Up to 25 x 200 ml. wide-mouth screw-cap polyethylene bottles for alkalinity determinations.