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MANUAL OF OCEANOGRAPHIC METHODS

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Editor

John P. Tully

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MANUAL OF
OCEANOGRAPHIC METHODS

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Foreword

This volume is presented in partial fulfillment of the requirement for a collection of seaworthy oceanographic methods, which was voiced at the Seventh Pacific Science Congress. To date oceanographic methods have been buried in personal handbooks, and class instructions in the several oceanographic institutions, and are not readily available to the oceanographic world. These methods have been compiled from the scientific literature, modified by experience in this Group and the Oceanographical Laboratories of the University of Washington to suit the sea-going oceanographer.

No doubt there are other acceptable methods for the tests discussed, and many tests have been omitted. We hope to improve this in subsequent editions.

These methods were mimeographed for the first class in Oceanographic Chemistry under the Institute of Oceanography at the University of British Columbia (I.O.U.B.C.).

John P. Tully
Oceanographer in Charge

List of Authors
(cf. reference number on each article)

1. Thompson, Thomas G.
   Director, Oceanographic Laboratories, University of Washington, Seattle, Washington

2. Robinson, Rex J.,
   Chemistry Professor, University of Washington, Seattle, Washington.

3. Barnes, Clifford A.
   Oceanography Professor, University of Washington

4. Hollister, Henry J.
   Senior Technician, Pacific Oceanographic Group, Nanaimo, B.C., Canada

5. Waldie, Robert J.
   Assistant Oceanographer, Pacific Oceanographic Group

6. Fjarlie, Robin L.I.
   Assistant Oceanographer, Pacific Oceanographic Group

7. Doe, L.A. Earlston
   Assistant Oceanographer, Pacific Oceanographic Group

8. Tully, John P.
   Oceanographer in Charge, Pacific Oceanographic Group

9. Carter, Neal M.
   Director, Fisheries Experimental Station, Vancouver

Contents

Preliminary Instructions in Oceanographic Chemistry (8)

Oceanographic measurements of the properties of sea water are generally concerned with small differences in large numbers, which implies a high degree of precision in the sampling and the analyses. The measurements are generally made by chemical methods because these are more precise than the physical methods, and more adaptable to the primitive laboratory conditions on board a ship at sea.

Calculations of ocean currents are cognizant of differences of salinity of the order of 0.01 to 0.05 °/oo, which implies that the accuracy of routine analyses must be within 0.3 % (1:3000). Under the conditions of work at sea this precision is only obtainable if the best techniques are employed.

It is usual to compare oceanographic data from all parts of the world, and over long periods of time to determine differences in regions of the sea, and trends and cycles with the seasons and the years. Therefore the analyses must be based on absolute, rather than relative standards. All the tables, and formulae of oceanography are empirical, based on careful measurements in terms of absolute standards. Therefore the weight basis of analyses must be referred to absolute standards, rather than the relative standards customarily employed in analytical procedure.

For example, the chlorinity of a sample could be determined on any other basis than absolute grams, only if a new empirical relation between chlorosity and chlorinity based on the new unit were devised.

It follows that it is a prerequisite of oceanographic chemistry that all apparatus be of good quality and be standardized, that the set-up be rugged, and adapted to making a large number of determinations with the minimum effort, the minimum quantity of materials, and without heat.

The following instructions are minimum preparation for operational oceanographic chemistry.

Notes

Cleanliness

All apparatus must be chemically clean. This implies that when the apparatus has dried droplets of (distilled) water will not adhere to the glass surface. They should spread over the surface in a uniform film.

Clean everything by vigorous brushing with a good detergent powder (Dutch Cleanser) rinsing repeatedly, and storing full of distilled water. This applies to burettes, measuring flasks, titrations flasks, etc.

To store a clean burette fill with water, insert a tight fitting cork in the upper end, and push it in as the stopcock is opened. Lay it on its side.

Pipettes may be cleaned by rinsing with NaOH - Alcohol cleaning solution, followed by two rinses with 0.1N HCl, and repeated rinses with fresh, then distilled water. When storing fit a short piece of rubber tubing over the upper end, fill the pipette with distilled water, close the tubing with a pinchcock, and lay on its side.

Seawater dissolves grease, therefore do not lubricate stopcocks which are situated above a clean region of apparatus, e.g. do not lubricate the stopcock of an automatic pipette.

Beakers used for dissolving standards must be chemically clean, and provided with equally clean stirring rods and cover glasses. The technique of transferring standards to measuring flasks is outlined in analytical chemistry texts, and must be rigidly followed.

Weights

Standard weights are the basis of all analysis. The procedure for standardising a set of weights is outlined in the analytical chemistry texts. In addition the 50, 20, 10, 5, and 1 gram weights are to be compared to International standards.

Standard apparatus

The volume of measuring flasks, and the delivery of burettes must be standardised by weight with standard weights.

Instructions

1. Assemble a 25 ml. Squibb type automatic burette as illustrated. Fire polish all glass ends. Clean the apparatus and store as instructed.

2. Make a Bunsen wash bottle.

3. Standardise a set of weights, in terms of international standards.

4. Standardise the 25 ml. burette every two ml. from 0 to 20 ml.
   Rate of delivery should be 95 ± 10 seconds for 25 ml. If necessary adjust to this limit by fire reducing the outlet, and filing the end flat.
   If the error of the burette exceeds 0.02 ml. standardise every 1 ml. If the error exceeds 0.05 ml. reject the burette.

5. Standardise the 250 ml. volumetric flasks, within 0.05 ml. This will require a community effort to standardise the trip balances to this precision.

6. Prepare two standard solutions of sodium chloride.
   Dry about 25 grams of analytical grade reagent, on which the lot analyses is known, at 110°C, cool in a dessicator at normal pressure. Accurately weigh (± 0.2 mgm.) 7 to 8 grams, dissolve in distilled water and make up accurately to about 250 ml. in distilled water.
   Store in a glass bottle with a waxed cork stopper.

7. Prepare standard solution of silver nitrate.
   Dissolve 97 grams of pure silver nitrate in two liters of distilled water. Store in a brown glass bottle.
   Silver chloride when freshly precipitated in the skin is soluble in 10 % sodium thiosulphate solution.

8. Prepare a solution of potassium chromate indicator.
   Dissolve 63 grams K_2CrO_4 in 100 ml. of boiling (distilled) water, cool to 20°C. Add 3 drops of silver nitrate solution, observe a red precipitate of Ag_2CrO_4, shake or stir thoroughly, and allow to settle. Filter through a fine filter (Whatman number 42). Store in a bottle with an eye dropper fitted through a waxed cork.

9. Prepare a standard solution of sodium thiosulphate.
   Dissolve 6 grams of the technical salt ($Na_2S_2O_3 . 5H_2O$) in two liters in fresh (tap) water. Add three drops carbon disulphide as preservative. Store in glass bottle with rubber stopper.

The Determination of the Chlorinity of Sea Water
(1,2,3,6,7,8)

The chlorinity is defined as the number of grams of halides calculated as chlorides in a kilogram of sea water. Its determination is of fundamental importance in all branches of oceanography, because it is the most convenient method for the expression of the concentration of a sample of sea water. All the physical properties of sea water are a function of the temperature, pressure, and concentration of the dissolved substances; thus, if the temperature and pressure are constant and the concentration varies, the change in physical properties will be a function of the concentration as expressed by the chlorinity.

The concentration of sea water is often expressed as the salinity which is calculated from the chlorinity. The salinity supposedly represents the total salts contained in a kilogram of sea water but is purely an arbitrary value.

The actual determination of the total amount of dissolved material is one of extreme analytical difficulty. Should a given volume or weight of sea water be evaporated with the idea of weighing the residue, it would be found that many chemical reactions will take place, such as the decomposition of bicarbonates with the loss of carbon dioxide, the hydrolysis of such salts as magnesium chloride and bromide, the possible volatilization of silicon tetrafluoride, the hydrolysis of silicates with the resulting dehydration of silicic acid, the change of primary and secondary phosphates to meta and pyro phosphates, respectively, the volatilization of boric acid, the loss of ammonia, etc. At the beginning of the present century, the oceanographic chemists had an appreciation of this difficulty, as did Robert Boyle two and one-half centuries ago. About 1900 an arbitrary term "salinity" was adopted to express the total weight in grams obtained by the evaporation of a kilogram of sea water after all the carbonates have been converted to oxides, the bromides and iodides replaced by chlorides, the organic matter completely oxidised, and the mass ignited at a temperature of 480°C. until constant weight has been obtained.

The salinity was found to be a function of the chlorinity expressible by

$$S = 0.030 + 1.805\, Cl\, {}^{\circ}/_{\circ\circ}$$

where *S* is the salinity and *Cl* is the chlorinity. Many oceanographers still use the term "salinity"; but for describing the concentration of the waters of the eastern Pacific, the term "chlorinity" is generally used. Two methods for its determination, both of marked accuracy, may be employed; namely, the Mohr and the Volhard methods. The errors of the determination of the former may be limited to one part in a thousand and, by means of weight titration, the Volhard method may be performed to an accuracy of one part in ten thousand, making it one of the most accurate of all determinations known in analytical chemistry. For the ordinary routine procedure, the Mohr method is universally used. Its accuracy is suitable for all practical purposes and the time required is considerably less than that of the Volhard procedure.

Standards for silver nitrate solutions

In order to have all the chlorinity or salinity determination comparable, the International Council for the Exploration of the Sea agreed upon a universal standard. This universal standard is a tube of sea water having a chlorinity approximating 19.38‰ obtainable at the Hydrographic Laboratories in Copenhagen. The water is collected from the sea for this particular purpose, and after preliminary standardization is passed into the clean, dry tubes of special glass which are then very carefully sealed so as to avoid any possible loss by evaporation of water. The chlorinity of the standard is determined by the Volhard method and generally every twentieth tube or so is opened at the Hydrographic Laboratories in Copenhagen and the ultimate chlorinity determined. When silver nitrate is to be standardized, the top of the tube is broken and samples of the standard water pipetted. It is bad practice to allow these tubes to stand after once open because of possible changes due to evaporation. This standard sea water should only be used for the standardization of silver nitrate solutions and under no circumstances should it be utilized as a standard for any other chemical procedure or physical measurement, as sometimes in the preparation of the standard water small quantities of potassium chloride are added in order to bring it to the required chlorinity.

During World War I, it became impossible to secure this standard water because of the submarine blockade. It was thus proposed by several European investigators to use pure sodium chloride as a standard, and the use of such standard was made the subject of special study by Thompson (Am. Chem. Soc. 50, 681, 1928). Sodium chloride is used in preference to potassium chloride because the atomic weight of sodium is known more accurately than that of potassium.

By use of the standard of the Hydrographic Laboratories, the titer tables in the Hydrographical tables of Knudsen are essential in order that the results be reported as grams of halide per kilogram of water.

It is obvious that a kilogram basis rather than that of volume is necessary because of its independence of temperature changes. The marked variation in the temperatures of the water and of the temperatures of the various laboratories throughout the world, in which the determinations would be performed, would lead to much confusion when comparisons of results were to be made on a volume basis.

If sodium chloride is to serve as a standard, the chlorinity per liter at the given temperature must be first determined, and from these results the chlorinity per kilo calculated. This is done by substitution in the empirical formula:

$$Cl_w = 0.008 + 0.99980\ Cl_v - 0.001228\ Cl_v^2$$

where Cl_w is the chlorinity per kilogram of water and Cl_v the chlorinity per liter at 20°C. In order to eliminate the calculations, the following table gives a means for conversion of chlorinity per liter to chlorinity per kilo, when the sea water sample is at or near the temperature of the standard silver nitrate. The table may be interpolated graphically as outlined in the reference.

Table I

Conversion of grams chloride per liter to
chlorinity (grams chloride per kilogram of sea water)

Chlorinity per liter	Temperature of sea water sample minus temperature of standard silver nitrate ($T_{Cl} - T_{Ag}$)				
	-5°C	-2.5°C	0°C	+2.5°C	+5°C
	Chlorinity per kilogram (Cl°/oo)				
1	0.999	1.000	1.000	1.001	1.002
2	1.996	1.997	1.998	1.999	2.000
3	2.990	2.991	2.993	2.995	2.996
4	3.981	3.983	3.985	3.987	3.990
5	4.970	4.972	4.975	4.978	4.981
6	5.956	5.958	5.962	5.965	5.969
7	6.939	6.942	6.946	6.950	6.955
8	7.919	7.923	7.928	7.932	7.938
9	8.897	8.902	8.907	8.912	8.918
10	9.873	9.878	9.883	9.889	8.896
11	10.846	10.851	10.857	10.864	10.872
12	11.816	11.822	11.829	11.837	11.845
13	12.784	12.791	12.798	12.806	12.815
14	13.750	13.756	13.765	13.774	13.782
15	14.713	14.720	14.729	14.738	14.748
16	15.673	15.681	15.690	15.701	15.711
17	16.631	16.639	16.650	16.661	16.672
18	17.587	17.595	17.606	17.618	17.630
19	18.540	18.549	18.561	18.573	18.586
20	19.490	19.500	19.513	19.526	19.539

Reference: H.M. Carter and J.P. Tully, Journal du Conseil
International pour l'Exploration de la Mer
Vol. XII, No. 1, pp. 36-39, 1939.

The Mohr Method

Chemistry of the method

Silver chloride has a solubility that is considerably less than that of silver chromate, so that silver chloride precipitates when silver nitrate is added to a solution containing both chloride and chromate ions. None of the silver chromate precipitates until all the chlorides have been removed from solution. (1) Silver chloride is white while silver chromate is red. Thus the first appearance of the red color, which in reality appears orange due to the yellow color imparted to the solution by the soluble chromate ions from the potassium chromate, indicates that all of the chlorides have been precipitated.

$$2\ Ag^+ + CrO_4^{=} \rightleftharpoons Ag_2CrO_4$$

$$Ag^+ + Cl^- \rightleftharpoons AgCl$$

Sufficient chromate ions must be present in the solution to insure precipitation of silver chromate. (2)

The method is only applicable between pH 4.5 and 9.0 and is most precise at neutrality. In the presence of a high concentration of hydrogen ions (pH less than 4.5).

$$H^+ + CrO_4^{=} \rightleftharpoons HCrO_4^-$$

and

$$2\ HCrO_4^- \rightleftharpoons Cr_2O_7^{=} + H_2O$$

the silver acid chromate is not precipitated. In other words, the hydrogen ion reduces the concentration of the chromate ions to such an extent that the solubility product of silver chromate is not exceeded.

On the other hand, if the hydrogen ion concentration is low (pH greater than 9.0), difficulty is experienced with the end point because of the marked tendency of the silver ions to precipitate as silver hydroxide, rather than as silver chloride or chromate.

The Solubility product

A slightly soluble substance suspended in water establishes equilibrium between the solid phase and the portion in solution. Since the concentration of the dissolved portion is extremely small, for all practical purposes it may be considered to be completely ionized.

$$\underset{(solid)}{A_mB_n} \rightleftharpoons \underset{(solu.)}{A_mB_n} \rightleftharpoons mA^+ + nB^- \qquad (1)$$

It follows from the law of mass action that

$$(A^+)^m \, (B^-)^n = K \, (A_mB_n) \qquad (2)$$

where the brackets denote the concentration of A and B as gram ions per liter and AB as gram molecules per liter, K is the ionization constant. As the solution is in equilibrium with the solid phase, the concentration of undissociated AB molecules in solution is a constant for a given temperature. Thus the equation (2) becomes

$$(A^+)^m \, (B^-)^n = K \, (A_mB_n) = Sp$$

where Sp is the solubility product. Thus the solubility product principle may be stated: In a saturated solution of a slightly soluble substance for a given temperature, the product of the ion concentrations, the concentration of each species being raised to a power equal to the number of ions of that species formed by the dissociation of one molecule of the substance, is equal to the constant. Practically it may be used to determine, if a precipitate will form or dissolve when ions are mixed together.

If the ionic product $(A^+)^m \, (B^-)^n$ becomes greater than Sp, precipitation results; if less, the suspended material goes into solution.

Procedure

Accurately pipette 10 ml. of sea water sample into a 125 ml. erlenmyer (conical) flask, dilute with 25 to 30 ml. of distilled water, add three drops of indicator and titrate with standard silver nitrate (from a 25 ml. burette) until a red color is obtained. Close the flask, with a tightly fitting rubber stopper and shake violently to break up the curds and liberate any soluble chlorides mechanically held. The red changes back to yellow in this operation. Remove the stopper and continue the titration to the chrome yellow end point, repeating the shaking technique at each approach to the end point.

Note that the suspended precipitate clears within 0.1 ml. of the end point, and at the end point the greenish yellow tinge changes sharply to chrome yellow.

Read the burette and apply burette and solution corrections to obtain chlorosity at temperature (t). Interpolate in Table I to determine chlorinity.

Reagents

Potassium chromate indicator

Saturated K_2CrO_4 solution, which contains 629 grams per liter.

Dissolve 63 grams K_2CrO_4 in 100 ml. of boiling (distilled) water, cool to 20°C. Add 3 drops silver nitrate (0.25N) observe a red precipitate of Ag_2CrO_4, shake or stir thoroughly, allow to settle. Filter through a fine filter(Whatman No. 42). Store in a bottle with an eye dropper fitted through a waxed cork.

Standard silver nitrate

Dissolve 48 grams of pure silver nitrate in one liter distilled water, and adjust concentration by dilution so that titer of a 10 ml. sample of the standard sodium chloride or sea water, at 20°C, equals the chlorosity within ± 0.05 ml.

It is desirable that the titer of the sea water sample at 20°C should be the chlorosity (grams chloride per liter) which may be derived:-

$$\begin{array}{c}\text{volume of equivalents}\\ \text{of silver nitrate}\end{array} = \begin{array}{c}\text{volume of equivalents}\\ \text{of chlorides}\end{array}$$

$$\frac{\text{Titer}}{1000} \times \frac{\text{wt. silver nitrate per liter}}{AgNO_3}$$

$$= \frac{\text{ml. sample}}{1000} \times \frac{\text{chlorosity}}{Cl}$$

Setting

$$\text{titer} = \text{chlorosity}$$

$$\begin{array}{l}\text{weight of silver nitrate}\\ \text{per liter}\end{array} = 4.7914 \times \text{ml. sample}$$

In the case of a 10 ml. sample the silver nitrate solution should be 0.2820 Normal.

Standard sodium chloride (primary standard)

A sodium chloride solution may be used as a primary standard. It is desirable that the chlorosity be about 18 g/l.

Dry about 25 grams of analytical grade, or repurified sodium chloride at 110°C, cool in a dessicator at normal pressure. Accurately weight (± 0.2 mgm.) 7 to 8 grams, dissolve in distilled water and make up accurately to about 250 ml. at 20°C.

Store in a glass bottle with waxed cork stopper.

The chlorosity of the standard sodium chloride is evaluated as

$$\frac{\text{grams chloride}}{1000} = \frac{\text{Cl}}{\text{NaCl}} \times \frac{\text{weight sodium chloride}}{\text{volume flask}} \times 1000 \times \frac{S_{20}}{S_t}$$

$$= 606.58 \times \frac{\text{Wt. NaCl}}{\text{Vol.Flask}} \times \frac{S_{20}}{S_t}$$

where S_{20} is the specific gravity of sea water at 20°C and S_t is the specific gravity of sea water at the temperature of titration, interpolated from Table II.

Table II

Specific Gravity of Sea Water (σt)

$\sigma t = (S_t - 1)\, 1000$

Temp. °C	Chlorosity (g/l) 16.00	17.00	18.00	19.00	20.00
			σt		
15	20.87	22.19	23.53	24.83	26.12
16	20.67	21.97	23.31	24.61	25.90
17	20.45	21.74	23.08	24.40	25.69
18	20.21	21.54	22.85	24.17	25.45
19	20.00	21.31	22.62	23.92	25.21
20	19.75	21.06	22.36	23.69	24.97
21	19.50	20.81	22.12	23.44	24.71
22	19.23	20.55	21.85	23.19	24.45
23	18.93	20.28	21.59	22.90	24.19
24	18.65	19.99	21.29	22.61	23.89
25	18.37	19.69	20.98	22.30	23.60

Correction for impurities in standard sodium chloride

Evidently the "weight of sodium chloride" to be substituted in the above equation must be the effective weight in the sample, which must be corrected for the impurities, calculated from the lot analyses.

Let 1 gram of reagent contain:

a grams of insoluble material
b grams of negative ions giving no precipitate with silver nitrate
c grams of positive ion impurity of equivalent weight C
e grams of positive ion impurity of equivalent weight E
. . . . etcetra . . . .

d grams negative ion impurity of equivalent weight D and which precipitates with silver nitrate.
f grams negative ion impurity of equivalent weight F and which precipitates with silver nitrate.
. . . . etcetra . . . .

h grams of soidum ion of equivalent weight Na
k grams of chlorine ion of equivalent weight Cl

Then

$$a + b + c + e + \ldots d + f + \ldots h + k = 1$$

The total number of chemical equivalents of positive ions per gram of reagent is

$$\frac{h}{Na} + \frac{c}{C} + \frac{e}{E} + \ldots .$$

This is equivalent to

$$\left(\frac{h}{Na} + \frac{c}{C} + \frac{e}{E} + \ldots .\right)Na$$

grams of sodium ion.

Similarly the total negative ion content is equivalent to

$$\left(\frac{k}{Cl} + \frac{d}{D} + \frac{f}{F} + \ldots .\right)Cl$$

grams of chlorine ion.

Therefore the quantity of NaCl which is equivalent to 1 gram of the reagent, so far as the titration with $AgNO_3$ is concerned, is:

$$\left(\frac{h}{Na} + \frac{c}{C} + \frac{e}{E} + \ldots\ldots\right)Na + \left(\frac{k}{Cl} + \frac{d}{D} + \frac{f}{F} + \ldots\ldots\right)Cl$$

which may be written:

$$h + k + \frac{CNa}{C} + \frac{eNa}{E} + \ldots\ldots + \frac{dCl}{D} + \frac{fCl}{F} + \ldots\ldots$$

Note that a and b have no part in the reaction and do not enter the equivalence function.

Therefore the correction to be applied per gram of reagent, is:

$$h + k + \frac{CNa}{C} + \ldots\ldots + \frac{dCl}{D} + \ldots\ldots - 1$$

$$= h + k + \frac{cNa}{C} + \ldots\ldots \frac{dCl}{D} + \ldots - (a+b+c+e \ldots +d+f+ \ldots +h+k)$$

$$= -(a+b) + \frac{c(Na-C)}{C} + \frac{e(Na-E)}{E} + \ldots \frac{d(Cl-D)}{D} + \frac{f(Cl-F)}{F} + \ldots$$

Standard sea water (secondary standard)

Filter one or two liters of sea water, and store in a glass bottle with a waxed cork stopper. Add one minute crystal of thymol to prevent bacterial growth.

This sea water is standardized against freshly standardized silver nitrate and used frequently to check the silver nitrate solution.

Standardization of the silver nitrate solution

1. Accurately determine the titer of a 10 ml. sample of primary standard, and a 10 ml. sample of secondary standard.

2. Calculate the theoretical titer of the II standard from the relation:

$$\frac{\text{theoretical titer I standard}}{\text{observed titer I standard}} = \frac{\text{theoretical titer II standard}}{\text{observed titer II standard}}$$

Use the secondary standard for manipulative standardizations.

3. It is desirable that the observed titer should be within 0.1 ml. of the theoretical titer in order to reduce subsequent calculations to a minimum.

The difference between the observed volume and the theoretical volume of the solution may be evaluated from the relation:

$$(\text{observed titer}) \times (\text{observed volume})$$

$$= (\text{theoretical titer}) \times (\text{theoretical volume})$$

It is advisable to make the silver nitrate solution a little too concentrated and subsequently dilute it to the theoretical concentration.

4. It is not practical or necessary to adjust the titer closer than 0.1 ml. of the theoretical value. Small differences are compensated by a correction table.

The corrections 0.01,0.02, 0.03, ... ml. are applied within limits specified by

$$N = (\text{theoretical titer}) - (\text{actual titer})$$

and

$$\text{correction interval} = \frac{2(\text{actual titer})}{(200N) + 1}$$

Example: A standard sodium chloride solution of chlorosity 18.65 cl/l. titrated with a silver nitrate solution, yields a titer of 18.60 ml. (including burette corrections). Therefore the solution correction

$$N = +0.05 \text{ ml.}$$

from which the correction interval is:

$$\frac{2 \times 18.60}{10 + 1} = \frac{37.20}{11} = 3.382 \text{ ml.}$$

whence the table of corrections is:

Titer limits (ml.)	Solution Correction
0.00 to 3.38	0.00 ml.
3.39 to 6.76	+ 0.01
6.77 to 10.14	+ 0.02
10.15 to 13.53	+ 0.03
13.54 to 16.91	+ 0.04
16.92 to 20.29	+ 0.05

5. Recalibrate the silver nitrate solution with secondary standard, making further adjustment if necessary. When the solution is apparently satisfactory, check accurately with the primary and secondary standards, and <u>inter se</u>.

Notes

1. From solubility tables it is observed that the solubility of silver chloride is less than that of silver chromate, yet on reference to the solubility product tables the value for silver chromate is considerably less than that of the chloride. However, comparison is being made between two different types of salts, AB and A_2D. Thus to compare AB with A_2D, the former should be considered as A_2B_2 and the solubility products should then be represented as follows:

$$(Ag^+)^2\ (Cl^-)^2 = K \quad (Ag^+)^2\ (CrO_4^=) = K_1$$

K is then less than K_1.

2. The chief sources of error in the method may be summarised as follows:

- (a) Failure to thoroughly stir or mix the solution during the process of titration in order to break up the curds of silver chloride.
- (b) The addition of insufficient quantities of the indicator. Three drops of the saturated solution of potassium chromate is sufficient to give a concentration so that the solubility product will be exceeded when just a portion of a drop of silver nitrate solution is added in excess. The end point correction is so small that it can be neglected.
- (c) Use of apparatus that fail to meet the specifications of the Bureau of Standards or the Hydrographic Laboratories.

3. The addition of the potassium chromate indicator imparts an intense yellow color to the sample being titrated. In order to nullify the effect of this color,better end points are obtained if the titration is conducted in artificial or yellow light rather~~m~~ than daylight.

4. It will be observed that in shaking the solution the curds of silver chloride are broken and the precipitate settles very rapidly. When an excess of silver chromate is obtained, violent shaking causes coagulation of the red precipitate, which likewise settles rapidly. If such a precipitate occurs it is easily visible and indicates that an excess of silver nitrate solution has been added.

5. Most neutral silver salts of the polybasic acids are insoluble and, as many of the salts of these acids are present in sea water, their precipitation would interfere with the method. However, calculations show that none of these salts occur in concentrations sufficient to cause precipitation of their silver salts. While the concentration of carbonates is relatively high, the bicarbonate ion is even considerably greater. However, silver bicarbonate does not precipitate with the conditions encountered and the solubility product of the silver carbonate is practically the same as that of silver chromate. Under the conditions of titration, the concentration of the chromate greatly exceeds that of the carbonates and, therefore, silver chromate tends to be precipitated first.

6. Because chlorinity is an absolute value of international acceptance the weights used must be standardised with accepted standards. The measuring flasks and burette must be standardised. It is not necessary to standardise the pipette since its correction is included in the solution correction.

7. Solutions stored in bottles with waxed cork stoppers do not "creep".

"Stew" the corks in hot paraffin wax for 3 to 5 minutes. Since the corks swell under this treatment use one size smaller than would normally be fitted.

Recovery of silver chloride

All silver residues are saved in suitable containers and the silver may be recovered and converted into silver nitrate again by the following procedure: The silver residues are dried and then mixed with about 25 per cent more than the theoretical amount of crude anhydrous sodium carbonate.

$$4\ AgCl + 2\ Na_2CO_3 \rightarrow 4\ NaCl + 2\ CO_2 + O_2 + 4\ Ag$$

The mixture is placed in a Hessian crucible and the latter set in an ordinary pot furnace heated by a large blast lamp. As the material reacts and melts, more of the mixture is added. The molten mass is finally poured into a suitable mould and on cooling the silver is readily separated from the slag. This silver is then remelted in the presence of powdered charcoal and poured as a fine stream into a large bucket of cold water. Silver flakes or shot are thus produced that are free from occluded sodium chloride, and after washing with water are dissolved in dilute nitric acid. The resulting solution is evaporated to dryness to remove excess acid. This is essential; otherwise it would be impossible to use a solution of the salt for titration, as the excess hydrogen ions from the nitric acid would prevent the formation of the silver chromate and thus obscure the endpoint.

$$Ag + NO_3^- + 2H^+ \rightarrow Ag^+ + NO_2 + H_2O \quad \text{(conc. acid)}$$

$$3\ Ag + NO_3^- + 4H^+ \rightarrow 3\ Ag^+ + NO + 2\ H_2O$$

The Volhard Method

The chemistry of the method

The soluble halides are precipitated with an excess of standard silver nitrate. The amount of the excess is then determined with a standard thiocyanate solution using ferric ion as the indicator. (1)

$$\mathrm{Ag^+ + Cl^- \rightleftharpoons AgCl}$$

$$\mathrm{Ag^+ + CNS^- \rightleftharpoons AgCNS}$$

The first appearance of a reddish brown tint to the solution indicates that the silver ion has completely reacted with the thiocyanate, and that there is a slight excess of the thiocyanate to react with the ferric ion. (2)

$$\mathrm{Fe^{+++} + 3\ CNS^- \longleftarrow Fe(CNS)_3}$$

$$\mathrm{Fe(CNS)_3 + 3\ CNS^- \longleftrightarrow Fe(\overset{red}{CNS})_6^{---}}$$

The precipitated silver chloride is removed by filtration before the excess silver ion is titrated because silver thiocyanate is more insoluble than silver chloride and a fading end point would otherwise be obtained. (3)

Reagents

Ferric Alum Indicator

One hundred ml. of a saturated solution of ferric ammonium alum is prepared. 5 ml. of nitric acid are added to prevent hydrolysis. (4)

Silver nitrate solution

Dissolve 97 grams of $\mathrm{AgNO_3}$ in 2 liters of distilled water and transfer to a glass-stoppered brown bottle.

Standard sodium chloride solution

Weigh 29.674 grams of pure NaCl and dilute to 1 liter.

Nitric acid

Concentrated C.P. nitric acid is diluted until it contains 50% nitric acid. It is then boiled free of oxides of nitrogen (5)

Ammonium thiocyanate solution

A 0.05 N solution is prepared by dissolving 4 grams of ammonium thiocyanate per liter.

Standardization of Silver Nitrate Solution

Determination of ratio of $AgNo_3/NH_4CNS$

Five ml. of the 50% nitric acid is added to a 10 ml. portion of silver nitrate, followed by 5 ml. of the ferric alum indicator. This solution is titrated with the ammonium thiocyanate solution until the reddish brown end point just persists after vigorous shaking. (6) The volume of silver nitrate divided by the volume of required ammonium thiocyanate gives the desired ratio.

Standardization of the silver nitrate solution

Pipet 10 ml. of the standard NaCl solution into a 150 ml. erlenmeyer flask. Add 5 ml. of nitric acid and 25 ml. of the silver nitrate solution. Heat to boiling and digest until the silver chloride is coagulated. (7) Let stand for six hours or longer. Filter and wash by decantation with a hot 1% nitric acid solution until the precipitate is free from occluded silver ion. Evaporate the collected filtrate and washings until the volume is no more than a 100 ml. Add 5 ml. of ferric alum solution and titrate with the thiocyanate solution. The normality of the silver nitrate may be calculated thus:

$$\frac{(10)\quad(29.674)}{(1000)\quad(\text{NaCl})} = (\text{ml. } AgNO_3)\ (N) - (\text{ml. } CNS^-)\ (AgNO_3/CNS^- \text{ ratio})$$

Procedure

A 10 ml. sample of sea water which has been filtered through Whatman No. 42 filter paper is treated with 5 ml. of nitric acid and then 25 ml. of the standard silver nitrate solution. The remainder of the procedure is made in the same manner as for the standardization of the silver nitrate solution. The calculation of the chlorinity per liter is made thus:

$$\frac{\left[25 - (\text{ml. } CNS^-)(AgNO_3/CNS^- \text{ ratio})\right]\ (0.2820)(35.46)(1000)}{(1000)\ (10)} = \text{Cl per liter}$$

where 0.2820 is equal to the normality of the silver nitrate solution and 35.46 is equal to the atomic weight of chlorine.

Notes

1. The original literature concerning the Volhard method may be found in Liebig's Ann d. Chem. <u>190</u>, 1 and Z. Anorg. Chem., <u>63</u> 330 (1909).

2. After a thorough experimental investigation the reddish brown color of the end point has been decided to be due to the complex ion $Fe(CNS)_6^{---}$ and not due to the $Fe(CNS)_3$ molecule as originally thought.

3. The solubility product for AgCl is 0.6×10^{-10} and for AgCNS is 0.6×10^{-12}. Since the silver thiocyanate is the more insoluble of the two, the excess CNS^- necessary to react with the ferric ion to give the end point would instead displace the chlorine from the silver chloride thus:

$$AgCl + CNS^- = AgCNS \quad Cl^-$$

The chlorine would then react with more silver ion. In practice a fading end point is obtained when the excess silver ion is titrated in the presence of the insoluble silver chloride. The following calculation shows that equilibrium would be attained when a ratio of Cl/CNS of 100 was obtained.

Since $(Ag^+)(Cl^-) = 0.6 \times 10^{-10}$ (1)
And $(Ag^+)(CNS^-) = 0.6 \times 10^{-12}$ (2)
At equilibrium the silver ion concentration
must be the same in either equation. So
when equation (1) is divided by equation (2)
the ratio of $(Cl^-)/(CNS^-) = 10^2$

Obviously this would be an impossible situation for a quantitative determination and so filtration of the silver chloride is necessary.

4. Nitric acid is added to the indicator solution to prevent hydrolysis as

$$Fe^{+++} + 3\,H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

The presence of the acid reverses this reaction.

5. The nitric acid is freed from the oxides of nitrogen since they too react with thiocyanate to give a red coloration.

6. The silver chloride is first formed in the colloidal state but is easily coagulated by heating in an acid solution.

7. Silver thiocyanate absorbs silver ion which is removed by vigorous shaking at the end point.

8. It has been demonstrated that the filtration of silver chloride is not necessary, providing 5 ml. of nitrobenzene are added to the solution, prior to titration with ammonium thiocyanate. (Caldwell and Moyer. Ind. Eng. Chem. <u>Anal</u>. <u>Ed</u>. 7, 38 (1935).)

These Tables were Copied from the

HYDROGRAPHICAL TABLES

edited by

MARTIN KNUDSEN

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FORMULAE AND EXPLANATION OF THE TABLES

Cl°/₀₀ means the amount of chlorine in °/₀₀, that is to say, the weight of chlorine in grams, found in 1000 grams of sea-water.

S°/₀₀ means the salinity in °/₀₀, that is to say, the total weight of salt in grams, found in 1000 grams of sea-water.
$S = 0.030 + 1.8050\,Cl.$

$\sigma_0 = (S_0 - 1)\,1000$, where S_0 means the specific gravity of sea-water at 0° referred to distilled water at 4°
$\sigma_0 = -0.069 + 1.4708\,Cl - 0.001570\,Cl^2 + 0.0000398\,Cl^3.$

$\rho_{17.5} = \left(\frac{S_{17.5}}{S_{17.5}} - 1\right)1000$, where $S_{17.5}$ means the specific gravity of sea-water at 17°.5 referred to distilled water at 4° and $S_{17.5}$ means the specific gravity of distilled water at 17°.5 in proportion to distilled water at 4°. Thus

$$\frac{S_{17.5}}{S_{17.5}} = S\left(\frac{17.5}{17.5}\right)$$

means the specific gravity of sea-water at 17°.5 referred to distilled water of the same temperature.
$\rho_{17.5} = (0.1245 + \sigma_0 - 0.0595\,\sigma_0 + 0.000155\,\sigma_0^2) \times 1.00129.$

Pacific Oceanographic Group
June, 1948.

$\mathrm{Cl}\,^0/_{00}$	$\mathrm{S}\,^0/_{00}$	σ_0	$\rho_{17.5}$	$\mathrm{Cl}\,^0/_{00}$	$\mathrm{S}\,^0/_{00}$	σ_0	$\rho_{17.5}$
1.00	1.84	1.40	1.44	1.50	2.74	2.13	2.13
.01	.85	.41	.46	.51	.76	.15	.15
.02	.87	.43	.47	.52	.77	.16	.16
.03	.89	.44	.48	.53	.79	.18	.18
.04	.91	.46	.50	.54	.81	.19	.19
.05	.93	.47	.51	.55	.83	.21	.20
.06	.94	.49	.53	.56	.85	.22	.22
.07	.96	.50	.54	.57	.86	.24	.23
.08	.98	.52	.55	.58	.88	.25	.25
.09	2.00	.53	.57	.59	.90	.27	.26
1.10	2.02	1.55	1.58	1.60	2.92	2.28	2.27
.11	.03	.56	.60	.61	.94	.30	.29
.12	.05	.58	.61	.62	.95	.31	.30
.13	.07	.59	.62	.63	.97	.32	.31
.14	.09	.61	.64	.64	.99	.34	.33
.15	.11	.62	.65	.65	3.01	.35	.34
.16	.12	.64	.66	.66	.03	.37	.36
.17	.14	.65	.68	.67	.04	.38	.37
.18	.16	.66	.69	.68	.06	.40	.38
.19	.18	.68	.71	.69	.08	.41	.40
1.20	2.20	1.69	1.72	1.70	3.10	2.43	2.41
.21	.21	.71	.73	.71	.12	.44	.42
.22	.23	.72	.75	.72	.13	.46	.44
.23	.25	.74	.76	.73	.15	.47	.45
.24	.27	.75	.78	.74	.17	.49	.47
.25	.29	.77	.79	.75	.19	.50	.48
.26	.30	.78	.80	.76	.21	.51	.49
.27	.32	.80	.82	.77	.22	.53	.51
.28	.34	.81	.83	.78	.24	.54	.52
.29	.36	.83	.84	.79	.26	.56	.54
1.30	2.38	1.84	1.86	1.80	3.28	2.57	2.55
.31	.39	.86	.87	.81	.30	.59	.56
.32	.41	.87	.89	.82	.32	.60	.58
.33	.43	.88	.90	.83	.33	.62	.59
.34	.45	.90	.91	.84	.35	.63	.60
.35	.47	.91	.93	.85	.37	.65	.62
.36	.48	.93	.94	.86	.39	.66	.63
.37	.50	.94	.95	.87	.41	.68	.65
.38	.52	.96	.97	.88	.42	.69	.66
.39	.54	.97	.98	.89	.44	.71	.67
1.40	2.56	1.99	2.00	1.90	3.46	2.72	2.69
.41	.58	2.00	.01	.91	.48	.73	.70
.42	.59	.02	.02	.92	.50	.75	.71
.43	.61	.03	.04	.93	.51	.76	.73
.44	.63	.05	.05	.94	.53	.78	.74
.45	.65	.06	.07	.95	.55	.79	.76
.46	.67	.08	.08	.96	.57	.81	.77
.47	.68	.09	.09	.97	.59	.82	.78
.48	.70	.10	.11	.98	.60	.84	.80
.49	.72	.12	.12	.99	.62	.85	.81

Cl°/₀₀	S°/₀₀	σ_0	$\rho_{17.5}$	Cl°/₀₀	S°/₀₀	σ_0	$\rho_{17.5}$
2.00	3.64	2.87	2.83	2.50	4.54	3.60	3.52
.01	.66	.88	.84	.51	.56	.61	.53
.02	.68	.90	.85	.52	.58	.63	.54
.03	.69	.91	.87	.53	.60	.64	.56
.04	.71	.93	.88	.54	.61	.66	.57
.05	.73	.94	.89	.55	.63	.67	.58
.06	.75	.96	.91	.56	.65	.69	.60
.07	.77	.97	.92	.57	.67	.70	.61
.08	.78	.98	.94	.58	.69	.72	.63
.09	.80	3.00	.95	.59	.70	.73	.64
2.10	3.82	3.01	2.96	2.60	4.72	3.75	3.65
.11	.84	.03	.98	.61	.74	.76	.67
.12	.86	.04	.99	.62	.76	.77	.68
.13	.87	.06	3.00	.63	.78	.79	.70
.14	.89	.07	.02	.64	.80	.80	.71
.15	.91	.09	.03	.65	.81	.82	.72
.16	.93	.10	.05	.66	.83	.83	.74
.17	.95	.12	.06	.67	.85	.85	.75
.18	.96	.13	.07	.68	.87	.86	.76
.19	.98	.14	.09	.69	.89	.88	.78
2.20	4.00	3.16	3.10	2.70	4.90	3.89	3.79
.21	.02	.17	.12	.71	.92	.91	.80
.22	.04	.19	.13	.72	.94	.92	.82
.23	.06	.20	.14	.73	.96	.94	.83
.24	.07	.22	.16	.74	.98	.95	.85
.25	.09	.23	.17	.75	.99	.96	.86
.26	.11	.25	.18	.76	5.01	.98	.87
.27	.13	.26	.20	.77	.03	.99	.89
.28	.15	.28	.21	.78	.05	4.01	.90
.29	.16	.29	.23	.79	.07	.02	.92
2.30	4.18	3.31	3.24	2.80	5.08	4.04	3.93
.31	.20	.32	.25	.81	.10	.05	.94
.32	.22	.34	.27	.82	.12	.07	.96
.33	.24	.35	.28	.83	.14	.08	.97
.34	.25	.36	.29	.84	.16	.10	.98
.35	.27	.38	.31	.85	.17	.11	4.00
.36	.29	.39	.32	.86	.19	.13	.01
.37	.31	.41	.34	.87	.21	.14	.03
.38	.33	.42	.35	.88	.23	.15	.04
.39	.34	.44	.36	.89	.25	.17	.05
2.40	4.36	3.45	3.38	2.90	5.26	4.18	4.07
.41	.38	.47	.39	.91	.28	.20	.08
.42	.40	.48	.40	.92	.30	.21	.09
.43	.42	.50	.42	.93	.32	.23	.11
.44	.43	.51	.43	.94	.34	.24	.12
.45	.45	.53	.45	.95	.35	.26	.14
.46	.47	.54	.46	.96	.37	.27	.15
.47	.49	.55	.47	.97	.39	.29	.16
.48	.51	.57	.49	.98	.41	.30	.18
.49	.52	.58	.50	.99	.43	.32	.19

Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$	Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$
3.00	5.45	4.33	4.21	3.50	6.35	5.06	4.89
.01	.46	.34	.22	.51	.37	.08	.91
.02	.48	.36	.23	.52	.38	.09	.92
.03	.50	.37	.25	.53	.40	.11	.94
.04	.52	.39	.26	.54	.42	.12	.95
.05	.54	.40	.27	.55	.44	.13	.96
.06	.55	.42	.29	.56	.46	.15	.98
.07	.57	.43	.30	.57	.47	.16	.99
.08	.59	.45	.32	.58	.49	.18	5.00
.09	.61	.46	.33	.59	.51	.19	.02
3.10	5.63	4.48	4.34	3.60	6.53	5.21	5.03
.11	.64	.49	.36	.61	.55	.22	.05
.12	.66	.51	.37	.62	.56	.24	.06
.13	.68	.52	.39	.63	.58	.25	.07
.14	.70	.54	.40	.64	.60	.27	.09
.15	.72	.55	.41	.65	.62	.28	.10
.16	.73	.56	.43	.66	.64	.30	.11
.17	.75	.58	.44	.67	.65	.31	.13
.18	.77	.59	.45	.68	.67	.32	.14
.19	.79	.61	.47	.69	.69	.34	.16
3.20	5.81	4.63	4.48	3.70	6.71	5.36	5.17
.21	.82	.64	.49	.71	.73	.37	.18
.22	.84	.65	.51	.72	.74	.38	.20
.23	.86	.67	.52	.73	.76	.40	.21
.24	.88	.68	.54	.74	.78	.41	.23
.25	.90	.70	.55	.75	.80	.43	.24
.26	.91	.71	.56	.76	.82	.44	.25
.27	.93	.73	.58	.77	.83	.46	.27
.28	.95	.74	.59	.78	.85	.47	.28
.29	.97	.75	.61	.79	.87	.48	.29
3.30	5.99	4.77	4.62	3.80	6.89	5.50	5.31
.31	6.00	.78	.63	.81	.91	.51	.32
.32	.02	.80	.65	.82	.93	.53	.34
.33	.04	.81	.66	.83	.94	.54	.35
.34	.06	.83	.67	.84	.96	.56	.36
.35	.08	.84	.69	.85	.98	.57	.38
.36	.09	.86	.70	.86	7.00	.59	.39
.37	.11	.87	.72	.87	.02	.60	.41
.38	.13	.89	.73	.88	.03	.62	.42
.39	.15	.90	.74	.89	.05	.63	.43
3.40	6.17	4.92	4.76	3.90	7.07	5.65	5.45
.41	.19	.93	.77	.91	.09	.66	.46
.42	.20	.94	.78	.92	.11	.67	.47
.43	.22	.96	.80	.93	.12	.69	.49
.44	.24	.97	.81	.94	.14	.70	.50
.45	.26	.99	.83	.95	.16	.72	.52
.46	.28	5.00	.84	.96	.18	.73	.53
.47	.29	.02	.85	.97	.20	.75	.54
.48	.31	.03	.87	.98	.21	.76	.56
.49	.33	.05	.88	.99	.23	.78	.57

Cl °/₀₀	S °/₀₀	σ_0	$\rho_{17.5}$
4.00	7.25	5.79	5.58
.01	.27	.81	.60
.02	.29	.82	.61
.03	.30	.84	.63
.04	.32	.85	.64
.05	.34	.86	.65
.06	.36	.88	.67
.07	.38	.89	.68
.08	.39	.91	.69
.09	.41	.92	.71
4.10	7.43	5.94	5.72
.11	.45	.95	.74
.12	.47	.97	.75
.13	.48	.98	.76
.14	.50	6.00	.78
.15	.52	.01	.79
.16	.54	.03	.80
.17	.56	.04	.82
.18	.57	.05	.83
.19	.59	.07	.85
4.20	7.61	6.08	5.86
.21	.63	.10	.87
.22	.65	.11	.89
.23	.67	.13	.90
.24	.68	.14	.92
.25	.70	.16	.93
.26	.72	.17	.94
.27	.74	.19	.96
.28	.76	.20	.97
.29	.77	.21	.98
4.30	7.79	6.23	6.00
.31	.81	.24	.01
.32	.83	.26	.03
.33	.85	.27	.04
.34	.86	.29	.05
.35	.88	.30	.07
.36	.90	.32	.08
.37	.92	.33	.09
.38	.94	.35	.11
.39	.96	.36	.12
4.40	7.97	6.38	6.14
.41	.99	.39	.15
.42	8.01	.40	.16
.43	.03	.42	.18
.44	.04	.43	.19
.45	.06	.45	.20
.46	.08	.46	.22
.47	.10	.48	.23
.48	.12	.49	.24
.49	.13	.51	.26
4.50	8.15	6.52	6.27
.51	.17	.54	.29
.52	.19	.55	.30
.53	.21	.57	.31
.54	.22	.58	.33
.55	.24	.59	.34
.56	.26	.61	.35
.57	.28	.62	.37
.58	.30	.64	.38
.59	.31	.65	.40
4.60	8.33	6.67	6.41
.61	.35	.68	.42
.62	.37	.70	.44
.63	.39	.71	.45
.64	.41	.73	.47
.65	.42	.74	.48
.66	.44	.76	.49
.67	.46	.77	.51
.68	.48	.78	.52
.69	.50	.80	.53
4.70	8.51	6.81	6.55
.71	.53	.83	.56
.72	.55	.84	.58
.73	.57	.86	.59
.74	.59	.87	.60
.75	.60	.89	.62
.76	.62	.90	.63
.77	.64	.92	.64
.78	.66	.93	.66
.79	.68	.94	.67
4.80	8.69	6.96	6.69
.81	.71	.97	.70
.82	.73	.99	.71
.83	.75	7.00	.73
.84	.77	.02	.74
.85	.78	.03	.76
.86	.80	.05	.77
.87	.82	.06	.78
.88	.84	.08	.80
.89	.86	.09	.81
4.90	8.87	7.10	6.82
.91	.89	.12	.84
.92	.91	.13	.85
.93	.93	.15	.86
.94	.95	.16	.88
.95	.96	.18	.89
.96	.98	.19	.91
.97	9.00	.21	.92
.98	.02	.22	.93
.99	.04	.24	.95

Cl ‰	S ‰	σ_0	$\rho_{17.5}$	Cl ‰	S ‰	σ_0	$\rho_{17.5}$
5.00	9.06	7.25	6.96	5.50	9.96	7.89	7.65
.01	.07	.27	.97	.51	.98	.99	.66
.02	.09	.28	.99	.52	.99	8.01	.68
.03	.11	.29	7.00	.53	10.01	.02	.69
.04	.13	.31	.02	.54	.03	.04	.70
.05	.15	.32	.03	.55	.05	.05	.72
.06	.16	.34	.04	.56	.07	.07	.73
.07	.18	.35	.06	.57	.08	.08	.74
.08	.20	.37	.07	.58	.10	.10	.76
.09	.22	.38	.08	.59	.12	.11	.77
5.10	9.24	7.40	7.10	5.60	10.14	8.13	7.79
.11	.25	.41	.11	.61	.16	.14	.80
.12	.27	.43	.13	.62	.17	.15	.81
.13	.29	.44	.14	.63	.19	.17	.83
.14	.31	.46	.15	.64	.21	.18	.84
.15	.33	.47	.17	.65	.23	.20	.86
.16	.34	.48	.18	.66	.25	.21	.87
.17	.36	.50	.19	.67	.26	.23	.88
.18	.38	.51	.21	.68	.28	.24	.90
.19	.40	.53	.22	.69	.30	.26	.91
5.20	9.42	7.54	7.24	5.70	10.32	8.27	7.93
.21	.43	.56	.25	.71	.34	.29	.94
.22	.45	.57	.26	.72	.35	.30	.95
.23	.47	.59	.28	.73	.37	.31	.97
.24	.49	.60	.29	.74	.39	.33	.98
.25	.51	.62	.30	.75	.41	.34	.99
.26	.52	.63	.32	.76	.43	.36	8.01
.27	.54	.64	.33	.77	.44	.37	.02
.28	.56	.66	.35	.78	.46	.39	.03
.29	.58	.67	.36	.79	.48	.40	.05
5.30	9.60	7.69	7.37	5.80	10.50	8.42	8.06
.31	.61	.70	.39	.81	.52	.43	.08
.32	.63	.72	.40	.82	.54	.45	.09
.33	.65	.73	.42	.83	.55	.46	.10
.34	.67	.75	.43	.84	.57	.47	.12
.35	.69	.76	.44	.85	.59	.49	.13
.36	.70	.78	.46	.86	.61	.50	.14
.37	.72	.79	.47	.87	.63	.52	.16
.38	.74	.80	.48	.88	.64	.53	.17
.39	.76	.82	.50	.89	.66	.55	.19
5.40	9.78	7.83	7.51	5.90	10.68	8.56	8.20
.41	.80	.85	.53	.91	.70	.58	.21
.42	.81	.86	.54	.92	.72	.59	.23
.43	.83	.88	.55	.93	.73	.61	.24
.44	.85	.89	.57	.94	.75	.62	.25
.45	.87	.91	.58	.95	.77	.64	.27
.46	.89	.92	.59	.96	.79	.65	.28
.47	.90	.94	.61	.97	.81	.66	.30
.48	.92	.95	.62	.98	.82	.68	.31
.49	.94	.97	.64	.99	.84	.69	.32

Cl°/	S°/	σ	$\rho_{17.5}$	Cl°/	S°/	σ	$\rho_{17.5}$
6.00	10.86	8.71	8.34	6.50	11.76	9.44	9.02
.01	.88	.72	.35	.51	.78	.45	.04
.02	.90	.74	.36	.52	.80	.46	.05
.03	.91	.75	.38	.53	.82	.48	.07
.04	.93	.77	.39	.54	.83	.49	.08
.05	.95	.78	.41	.55	.85	.51	.09
.06	.97	.80	.42	.56	.87	.52	.11
.07	.99	.81	.43	.57	.89	.54	.12
.08	11.00	.82	.45	.58	.91	.55	.13
.09	.02	.84	.46	.59	.92	.57	.15
6.10	11.04	8.85	8.47	6.60	11.94	9.58	9.16
.11	.06	.87	.49	.61	.96	.60	.18
.12	.08	.88	.50	.62	.98	.61	.19
.13	.09	.90	.52	.63	12.00	.62	.20
.14	.11	.91	.53	.64	.02	.64	.22
.15	.13	.93	.54	.65	.03	.65	.23
.16	.15	.94	.56	.66	.05	.67	.24
.17	.17	.96	.57	.67	.07	.68	.26
.18	.18	.97	.58	.68	09	.70	.27
.19	.20	.98	.60	.69	.11	.71	.29
6.20	11.22	9.00	8.61	6.70	12.12	9.73	9.30
.21	.24	.01	.63	.71	.14	.74	.31
.22	.26	.03	.64	.72	.16	.76	.33
.23	.28	.04	.65	.73	.18	.77	.34
.24	.29	.06	.67	.74	.20	.79	.35
.25	.31	.07	.68	.75	.21	.80	.37
.26	.33	.09	.69	.76	.23	.81	.38
.27	.35	.10	.71	.77	.25	.83	.39
.28	.37	.12	.72	.78	.27	.84	.41
.29	.38	.13	.74	.79	.29	.86	.42
6.30	11.40	9.14	8.75	6.80	12.30	9.87	9.44
.31	.42	.16	.76	.81	.32	.89	.45
.32	.44	.17	.78	.82	.34	.90	.46
.33	.46	.19	.79	.83	.36	.92	.48
.34	.47	.20	.80	.84	.38	.93	.49
.35	.49	.22	.82	.85	.39	.95	.51
.36	.51	.23	.83	.86	.41	.96	.52
.37	.53	.25	.85	.87	.43	.97	.53
.38	.55	.26	.86	.88	.45	.99	.55
.39	.56	.28	.87	.89	.47	10.00	.56
6.40	11.58	9.29	8.89	6.90	12.48	10.02	9.57
.41	.60	.30	.90	.91	.50	.03	.59
.42	.62	.32	.91	.92	.52	.05	.60
.43	.64	.33	.93	.93	.54	.06	.62
.44	.65	.35	.94	.94	.56	.08	.63
.45	.67	.36	.96	.95	.57	.09	.64
.46	.69	.38	.97	.96	.59	.11	.66
.47	.71	.39	.98	.97	.61	.12	.67
.48	.73	.41	9.00	.98	.63	.13	.68
.49	.74	.42	.01	.99	.65	.15	.70

Cl°/	S°/	σ	$\rho_{17.5}$	Cl°/	S°/	σ	$\rho_{17.5}$
7.00	12.67	10.16	9.71	7.50	13.57	10.89	10.40
.01	.68	.18	.72	.51	.59	.91	.41
.02	.70	.19	.74	.52	.60	.92	.43
.03	.72	.21	.75	.53	.62	.93	.44
.04	.74	.22	.77	.54	.64	.95	.45
.05	.76	.24	.78	.55	.66	.96	.47
.06	.77	.25	.79	.56	.68	.98	.48
.07	.79	.27	.81	.57	.69	.99	.49
.08	.81	.28	.82	.58	.71	11.01	.51
.09	.83	.29	.84	.59	.73	.02	.52
7.10	12.85	10.31	9.85	7.60	13.75	11.04	10.54
.11	.86	.32	.86	.61	.77	.05	.55
.12	.88	.34	.88	.62	.78	.06	.56
.13	.90	.35	.89	.63	.80	.08	.58
.14	.92	.37	.90	.64	.82	.09	.59
.15	.94	.38	.92	.65	.84	.11	.60
.16	.96	.40	.93	.66	.86	.12	162
.17	.97	.41	.94	.67	.87	.14	.63
.18	.99	.43	.96	.68	.89	.15	.65
.19	13.01	.44	.97	.69	.91	.17	.66
7.20	13.03	10.46	9.99	7.70	13.93	11.18	10.67
.21	.04	.47	10.00	.71	.95	.20	.69
.22	.06	.48	.01	.72	.96	.21	.70
.23	.08	.50	.03	.73	.98	.23	.71
.24	.10	.51	.04	.74	14.00	.24	.73
.25	.12	.53	.06	.75	.02	.25	.74
.26	.13	.54	.07	.76	.04	.27	.76
.27	.15	.56	.08	.77	.05	.28	.77
.28	.17	.57	.10	.78	.07	.30	.78
.29	.19	.59	.11	.79	.09	.31	.80
7.30	13.21	10.60	10.12	7.80	14.11	11.33	10.81
.31	.22	.61	.14	.81	.13	.34	.82
.32	.24	.63	.15	.82	.15	.36	.84
.33	.26	.64	.17	.83	.16	.37	.85
.34	.28	.66	.18	.84	.18	.38	.87
.35	.30	.67	.19	.85	.20	.40	.88
.36	.31	.69	.21	.86	.22	.41	.89
.37	.33	.70	.22	.87	.24	.43	.91
.38	.35	.72	.23	.88	.25	.44	.92
.39	.37	.73	.25	.89	.27	.46	.93
7.40	13.39	10.75	10.26	7.90	14.29	11.47	10.95
.41	.41	.76	.27	.91	.31	.49	.96
.42	.42	.77	.29	.92	.33	.50	.98
.43	.44	.79	.30	.93	.34	.52	.99
.44	.46	.80	.32	.94	.36	.53	11.00
.45	.48	.82	.33	.95	.38	.54	.02
.46	.50	.83	.34	.96	.40	.56	.03
.47	.51	.85	.36	.97	.42	.57	.04
.48	.53	.86	.37	.98	.43	.59	.06
.49	.55	.88	.38	.99	.45	.60	.07

Cl°/	S°/	σ	$\sigma_{17.5}$	Cl°/	S°/	σ	$\sigma_{17.5}$
8.00	14.47	11.62	11.09	8.50	15.37	12.34	11.77
.01	.49	.63	.10	.51	.39	.36	.79
.02	.51	.65	.11	.52	.41	.37	.80
.03	.52	.66	.13	.53	.43	.39	.81
.04	.54	.68	.14	.54	.44	.40	.83
.05	.56	.69	.16	.55	.46	.42	.84
.06	.58	.70	.17	.56	.48	.43	.86
.07	.60	.72	.18	.57	.50	.45	.87
.08	.61	.73	.20	.58	.52	.46	.88
.09	.63	.75	.21	.59	.53	.47	.90
8.10	14.65	11.76	11.22	8.60	15.55	12.49	11.91
.11	.67	.78	.24	.61	.57	.50	.92
.12	.69	.79	.25	.62	.59	.52	.94
.13	.70	.81	.26	.63	.61	.53	.95
.14	.72	.82	.28	.64	.63	.55	.96
.15	.74	.84	.29	.65	.64	.56	.98
.16	.76	.85	.31	.66	.66	.58	.99
.17	.78	.86	.32	.67	.68	.59	12.01
.18	.79	.88	.33	.68	.70	.61	.02
.19	.81	.89	.35	.69	.72	.62	.03
8.20	14.83	11.91	11.36	8.70	15.73	12.63	12.05
.21	.85	.92	.37	.71	.75	.65	.06
.22	.87	.94	.39	.72	.77	.66	.07
.23	.89	.95	.40	.73	.79	.68	.09
.24	.90	.97	.42	.74	.81	.69	.10
.25	.92	.98	.43	.75	.82	.71	.12
.26	.94	12.00	.44	.76	.84	.72	.13
.27	.96	.01	.46	.77	.86	.74	.14
.28	.98	.02	.47	.78	.88	.75	.16
.29	.99	.04	.48	.79	.90	.77	.17
8.30	15.01	12.05	11.50	8.80	15.91	12.78	12.19
.31	.03	.07	.51	.81	.93	.79	.20
.32	.05	.08	.53	.82	.95	.81	.21
.33	.07	.10	.54	.83	.97	.82	.23
.34	.08	.11	.55	.84	.99	.84	.24
.35	.10	.13	.57	.85	16.00	.85	.25
.36	.12	.14	.58	.86	.02	.87	.27
.37	.14	.15	.59	.87	.04	.88	.28
.38	.16	.17	.61	.88	.06	.90	.29
.39	.17	.18	.62	.89	.08	.91	.31
8.40	15.19	12.20	11.64	8.90	16.09	12.93	12.32
.41	.21	.21	.65	.91	.11	.94	.34
.42	.23	.23	.66	.92	.13	.95	.35
.43	.25	.24	.68	.93	.15	.97	.36
.44	.26	.26	.69	.94	.17	.98	.38
.45	.28	.27	.70	.95	.18	13.00	.39
.46	.30	.29	.72	.96	.20	.01	.40
.47	.32	.30	.73	.97	.22	.03	.42
.48	.34	.31	.75	.98	.24	.04	.43
.49	.35	.33	.76	.99	.26	.06	.45

Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$	Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$
9.00	16.28	13.07	12.46	9.50	17.18	13.80	13.15
.01	.29	.08	.47	.51	.20	.81	.16
.02	.31	.10	.49	.52	.21	.83	.17
.03	.33	.11	.50	.53	.23	.84	.19
.04	.35	.13	.51	.54	.25	.85	.20
.05	.37	.14	.53	.55	.27	.87	.21
.06	.38	.16	.54	.56	.29	.88	.23
.07	.40	.17	.56	.57	.30	.90	.24
.08	.42	.19	.57	.58	.32	.91	.26
.09	.44	.20	.58	.59	.34	.93	.27
9.10	16.46	13.22	12.60	9.60	17.36	13.94	13.28
.11	.47	.23	.61	.61	.38	.96	.30
.12	.49	.24	.62	.62	.39	.97	.31
.13	.51	.26	.64	.63	.41	.98	.32
.14	.53	.27	.65	.64	.43	14.00	.34
.15	.55	.29	.67	.65	.45	.01	.35
.16	.56	.30	.68	.66	.47	.03	.37
.17	.58	.32	.69	.67	.48	.04	.38
.18	.60	.33	.71	.68	.50	.06	.39
.19	.62	.35	.72	.69	.52	.07	.41
9.20	16.64	13.36	12.73	9.70	17.54	14.09	13.42
.21	.65	.37	.75	.71	.56	.10	.43
.22	.67	.39	.76	.72	.57	.12	.45
.23	.69	.40	.78	.73	.59	.13	.46
.24	.71	.42	.79	.74	.61	.14	.48
.25	.73	.43	.80	.75	.63	.16	.49
.26	.74	.45	.82	.76	.65	.17	.50
.27	.76	.46	.83	.77	.66	.19	.52
.28	.78	.48	.84	.78	.68	.20	.53
.29	.80	.49	.86	.79	.70	.22	.55
9.30	16.82	13.51	12.87	9.80	17.72	14.23	13.56
.31	.83	.52	.89	.81	.74	.25	.57
.32	.85	.53	.90	.82	.76	.26	.59
.33	.87	.55	.91	.83	.77	.28	.60
.34	.89	.56	.93	.84	.79	.29	.61
.35	.91	.58	.94	.85	.81	.30	.63
.36	.92	.59	.95	.86	.83	.32	.64
.37	.94	.61	.97	.87	.85	.33	.65
.38	.96	.62	.98	.88	.86	.35	.67
.39	.98	.64	13.00	.89	.88	.36	.68
9.40	17.00	13.65	13.01	9.90	17.90	14.38	13.70
.41	.02	.67	.02	.91	.92	.39	.71
.42	.03	.68	.04	.92	.94	.41	.72
.43	.05	.69	.05	.93	.96	.42	.74
.44	.07	.71	.06	.94	.97	.43	.75
.45	.09	.72	.08	.95	.99	.45	.76
.46	.11	.74	.09	.96	18.01	.46	.78
.47	.12	.75	.10	.97	.03	.48	.79
.48	.14	.77	.12	.98	.04	.49	.81
.49	.16	.78	.13	.99	.06	.51	.82

Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$	Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$
10.00	18.08	14.52	13.83	10.50	18.98	15.25	14.52
.01	.10	.54	.85	.51	19.00	.26	.53
.02	.12	.55	.86	.52	.02	.28	.55
.03	.13	.57	.87	.53	.04	.29	.56
.04	.15	.58	.89	.54	.05	.31	.57
.05	.17	.59	.90	.55	.07	.32	.59
.06	.19	.61	.92	.56	.09	.33	.60
.07	.21	.62	.93	.57	.11	.35	.61
.08	.23	.64	.94	.58	.13	.36	.63
.09	.24	.65	.96	.59	.14	.38	.64
10.10	18.26	14.67	13.97	10.60	19.16	15.39	14.66
.11	.28	.68	.98	.61	.18	.41	.67
.12	.30	.70	14.00	.62	.20	.42	.68
.13	.31	.71	.01	.63	.22	.44	.70
.14	.33	.72	.02	.64	.24	.45	.71
.15	.35	.74	.04	.65	.25	.47	.73
.16	.37	.75	.05	.66	.27	.48	.74
.17	.39	.77	.07	.67	.29	.49	.75
.18	.40	.78	.08	.68	.31	.51	.77
.19	.42	.80	.09	.69	.33	.52	.78
10.20	18.44	14.81	14.11	10.70	19.34	15.54	14.79
.21	.46	.83	.12	.71	.36	.55	.81
.22	.48	.84	.13	.72	.38	.57	.82
.23	.50	.86	.15	.73	.40	.58	.84
.24	.51	.87	.16	.74	.42	.60	.85
.25	.53	.88	.18	.75	.43	.61	.86
.26	.55	.90	.19	.76	.45	.62	.88
.27	.57	.91	.20	.77	.47	.64	.89
.28	.59	.93	.22	.78	.49	.65	.90
.29	.60	.94	.23	.79	.51	.67	.92
10.30	18.62	14.96	14.24	10.80	19.52	15.68	14.93
.31	.64	.97	.26	.81	.54	.70	.95
.32	.66	.99	.27	.82	.56	.71	.96
.33	.68	15.00	.29	.83	.58	.73	.97
.34	.69	.02	.30	.84	.60	.74	.99
.35	.71	.03	.31	.85	.61	.76	15.00
.36	.73	.04	.33	.86	.63	.77	.01
.37	.75	.06	.34	.87	.65	.78	.03
.38	.77	.07	.36	.88	.67	.80	.04
.39	.78	.09	.37	.89	.69	.81	.06
10.40	18.80	15.10	14.38	10.90	19.70	15.83	15.07
.41	.82	.12	.40	.91	.72	.84	.08
.42	.84	.13	.41	.92	.74	.86	.10
.43	.86	.15	.42	.93	.76	.87	.11
.44	.87	.16	.44	.94	.78	.89	.12
.45	.89	.17	.45	.95	.79	.90	.14
.46	.91	.19	.46	.96	.81	.91	.15
.47	.93	.20	.48	.97	.83	.93	.16
.48	.95	.22	.49	.98	.85	.94	.18
.49	.96	.23	.51	.99	.87	.96	.19

Cl‰	S‰	σ_0	$\rho_{17,5}$	Cl‰	S‰	σ_0	$\rho_{17,5}$
11.00	19.89	15.97	15.21	11.50	20.79	16.70	15.89
.01	.90	.99	.22	.51	.81	.71	.91
.02	.92	16.00	.23	.52	.82	.73	.92
.03	.94	.02	.25	.53	.84	.74	.93
.04	.96	.03	.26	.54	.86	.76	.95
.05	.98	.05	.27	.55	.88	.77	.96
.06	.99	.06	.29	.56	.90	.79	.98
.07	20.01	.07	.30	.57	.91	.80	.99
.08	.03	.09	.32	.58	.93	.81	16.00
.09	.05	.10	.33	.59	.95	.83	.01
11.10	20.07	16.12	15.34	11.60	20.97	16.84	16.03
.11	.08	.13	.36	.61	.99	.86	.04
.12	.10	.15	.37	.62	21.00	.87	.06
.13	.12	.16	.39	.63	.02	.89	.07
.14	.14	.18	.40	.64	.04	.90	.08
.15	.16	.19	.41	.65	.06	.92	.10
.16	.17	.20	.43	.66	.08	.93	.11
.17	.19	.22	.44	.67	.09	.94	.13
.18	.21	.23	.46	.68	.11	.96	.14
.19	.23	.25	.47	.69	.13	.97	.15
11.20	20.25	16.26	15.48	11.70	21.15	16.99	16.17
.21	.26	.28	.49	.71	.17	17.00	.18
.22	.28	.29	.51	.72	.18	.02	.19
.23	.30	.31	.52	.73	.20	.03	.21
.24	.32	.32	.54	.74	.22	.05	.22
.25	.34	.34	.55	.75	.24	.06	.24
.26	.35	.35	.56	.76	.26	.08	.25
.27	.37	.36	.58	.77	.27	.09	.26
.28	.39	.38	.59	.78	.29	.10	.28
.29	.41	.39	.60	.79	.31	.12	.29
11.30	20.43	16.41	15.62	11.80	21.33	17.13	16.30
.31	.44	.42	.63	.81	.35	.15	.32
.32	.46	.44	.65	.82	.37	.16	.33
.33	.48	.45	.66	.83	.38	.18	.35
.34	.50	.47	.67	.84	.40	.19	.36
.35	.52	.48	.69	.85	.42	.21	.37
.36	.53	.50	.70	.86	.44	.22	.39
.37	.55	.51	.71	.87	.46	.23	.40
.38	.57	.52	.73	.88	.47	.25	.41
.39	.59	.54	.74	.89	.49	.26	.43
11.40	20.61	16.55	15.76	11.90	21.51	17.28	16.44
.41	.63	.57	.77	.91	.53	.29	.46
.42	.64	.58	.78	.92	.55	.31	.47
.43	.66	.60	.80	.93	.56	.32	.48
.44	.68	.61	.81	.94	.58	.34	.50
.45	.70	.63	.82	.95	.60	.35	.51
.46	.72	.64	.84	.96	.62	.37	.52
.47	.73	.65	.85	.97	.64	.38	.54
.48	.75	.67	.87	.98	.65	.39	.55
.49	.77	.68	.88	.99	.67	.41	.57

Cl‰	S‰	σ_0	$\rho_{17.5}$	Cl‰	S‰	σ_0	$\rho_{17.5}$
12.00	21.69	17.42	16.58	12.50	22.59	18.15	17.27
.01	.71	.44	.59	.51	.61	.16	.28
.02	.73	.45	.61	.52	.63	.18	.29
.03	.74	.47	.62	.53	.65	.19	.31
.04	.76	.48	.63	.54	.66	.21	.32
.05	.78	.50	.65	.55	.68	.22	.33
.06	.80	.51	.66	.56	.70	.24	.35
.07	.82	.52	.68	.57	.72	.25	.36
.08	.83	.54	.69	.58	.74	.26	.38
.09	.85	.55	.70	.59	.75	.28	.39
12.10	21.87	17.57	16.72	12.60	22.77	18.29	17.40
.11	.89	.58	.73	.61	.79	.31	.42
.12	.91	.60	.74	.62	.81	.32	.43
.13	.92	.61	.76	.63	.83	.34	.44
.14	.94	.63	.77	.64	.85	.35	.46
.15	.96	.64	.79	.65	.86	.37	.47
.16	.98	.66	.80	.66	.88	.38	.49
.17	22.00	.67	.81	.67	.90	.39	.50
.18	.01	.68	.83	.68	.92	.41	.51
.19	.03	.70	.84	.69	.94	.42	.53
12.20	22.05	17.71	16.86	12.70	22.95	18.44	17.54
.21	.07	.73	.87	.71	.97	.45	.55
.22	.09	.74	.88	.72	.99	.47	.57
.23	.11	.76	.90	.73	23.01	.48	.58
.24	.12	.77	.91	.74	.03	.50	.60
.25	.14	.79	.92	.75	.04	.51	.61
.26	.16	.80	.94	.76	.06	.53	.62
.27	.18	.81	.95	.77	.08	.54	.64
.28	.20	.83	.96	.78	.10	.55	.65
.29	.21	.84	.98	.79	.12	.57	.66
12.30	22.23	17.86	16.99	12.80	23.13	18.58	17.68
.31	.25	.87	17.00	.81	.15	.60	.69
.32	.27	.89	.02	.82	.17	.61	.71
.33	.29	.90	.03	.83	.19	.63	.72
.34	.30	.92	.05	.84	.21	.64	.73
.35	.32	.93	.06	.85	.22	.66	.75
.36	.34	.95	.07	.86	.24	.67	.76
.37	.36	.96	.09	.87	.26	.68	.77
.38	.38	.97	.10	.88	.28	.70	.79
.39	.39	.99	.12	.89	.30	.71	.80
12.40	22.41	18.00	17.13	12.90	23.31	18.73	17.82
.41	.43	.02	.14	.91	.33	.74	.83
.42	.45	.03	.16	.92	.35	.76	.84
.43	.47	.05	.17	.93	.37	.77	.86
.44	.48	.06	.18	.94	.39	.79	.87
.45	.50	.08	.20	.95	.40	.80	.88
.46	.52	.09	.21	.96	.42	.82	.90
.47	.54	.10	.22	.97	.44	.83	.91
.48	.56	.12	.24	.98	.46	.84	.93
.49	.57	.13	.25	.99	.48	.86	.94

Cl°/₀₀	S°/₀₀	σ_0	$\sigma_{17.5}$	Cl°/₀₀	S°/₀₀	σ_0	$\sigma_{17.5}$
13.00	23.50	18.87	17.96	13.50	24.40	19.60	18.64
.01	.51	.89	.97	.51	.42	.61	.65
.02	.53	.90	.98	.52	.43	.63	.67
.03	.55	.92	.99	.53	.45	.64	.68
.04	.57	.93	18.01	.54	.47	.66	.70
.05	.59	.95	.02	.55	.49	.67	.71
.06	.60	.96	.04	.56	.51	.69	.72
.07	.62	.98	.05	.57	.52	.70	.74
.08	.64	.99	.06	.58	.54	.71	.75
.09	.66	19.00	.08	.59	.56	.73	.76
13.10	23.68	19.02	18.09	13.60	24.58	19.74	18.78
.11	.69	.03	.10	.61	.60	.76	.79
.12	.71	.05	.12	.62	.61	.77	.81
.13	.73	.06	.13	.63	.63	.79	.82
.14	.75	.08	.15	.64	.65	.80	.83
.15	.77	.09	.16	.65	.67	.82	.85
.16	.78	.11	.17	.66	.69	.83	.86
.17	.80	.12	.19	.67	.70	.85	.87
.18	.82	.13	.20	.68	.72	.86	.89
.19	.84	.15	.22	.69	.74	.87	.90
13.20	23.86	19.16	18.23	13.70	24.76	19.89	18.92
.21	.87	.18	.24	.71	.78	.90	.93
.22	.89	.19	.26	.72	.79	.92	.94
.23	.91	.21	.27	.73	.81	.93	.96
.24	.93	.22	.28	.74	.83	.95	.97
.25	.95	.24	.30	.75	.85	.96	.98
.26	.96	.25	.31	.76	.87	.98	19.00
.27	.98	.27	.32	.77	.88	.99	.01
.28	24.00	.28	.34	.78	.90	20.00	.03
.29	.02	.29	.35	.79	.92	.02	.04
13.30	24.04	19.31	18.37	13.80	24.94	20.03	19.05
.31	.06	.32	.38	.81	.96	.05	.07
.32	.07	.34	.39	.82	.98	.06	.08
.33	.09	.35	.41	.83	.99	.08	.09
.34	.11	.37	.42	.84	25.01	.09	.11
.35	.13	.38	.44	.85	.03	.11	.12
.36	.14	.40	.45	.86	.05	.12	.14
.37	.16	.41	.46	.87	.07	.14	.15
.38	.18	.42	.48	.88	.08	.15	.16
.39	.20	.44	.49	.89	.10	.16	.18
13.40	24.22	19.45	18.50	13.90	25.12	20.18	19.19
.41	.24	.47	.52	.91	.14	.19	.20
.42	.25	.48	.53	.92	.16	.21	.22
.43	.27	.50	.54	.93	.17	.22	.23
.44	.29	.51	.56	.94	.19	.24	.25
.45	.31	.53	.57	.95	.21	.25	.26
.46	.33	.54	.59	.96	.23	.27	.27
.47	.34	.56	.60	.97	.25	.28	.29
.48	.36	.57	.61	.98	.26	.29	.30
.49	.38	.58	.63	.99	.28	.31	.31

Cl°/..	S°/..	σ_0	$\rho_{17.5}$	Cl°/..	S°/..	σ_0	$\rho_{17.5}$
14.00	25.30	20.32	19.33	14.50	26.20	21.05	20.02
.01	.32	.34	.34	.51	.22	.06	.03
.02	.34	.35	.36	.52	.24	.08	.04
.03	.35	.37	.37	.53	.25	.09	.05
.04	.37	.38	.39	.54	.27	.11	.07
.05	.39	.40	.40	.55	.29	.12	.08
.06	.41	.41	.41	.56	.31	.14	.10
.07	.43	.43	.42	.57	.33	.15	.11
.08	.44	.44	.44	.58	.35	.16	.13
.09	.46	.45	.45	.59	.36	.18	.14
14.10	25.48	20.47	19.47	14.60	26.38	21.19	20.15
.11	.50	.48	.48	.61	.40	.21	.17
.12	.52	.50	.49	.62	.42	.22	.18
.13	.53	.51	.51	.63	.44	.24	.19
.14	.55	.53	.52	.64	.46	.25	.21
.15	.57	.54	.53	.65	.47	.27	.22
.16	.59	.56	.55	.66	.49	.28	.24
.17	.61	.57	.56	.67	.51	.30	.25
.18	.62	.58	.58	.68	.53	.31	.26
.19	.64	.60	.59	.69	.55	.32	.28
14.20	25.66	20.61	19.60	14.70	26.56	21.34	20.29
.21	.68	.63	.62	.71	.58	.35	.30
.22	.70	.64	.63	.72	.60	.37	.32
.23	.72	.66	.64	.73	.62	.38	.33
.24	.73	.67	.66	.74	.64	.40	.35
.25	.75	.69	.67	.75	.65	.41	.36
.26	.77	.70	.69	.76	.67	.43	.37
.27	.79	.72	.70	.77	.69	.44	.39
.28	.81	.73	.71	.78	.71	.45	.40
.29	.82	.74	.73	.79	.73	.47	.41
14.30	25.84	20.76	19.74	14.80	26.74	21.48	20.43
.31	.86	.77	.75	.81	.76	.50	.44
.32	.88	.79	.77	.82	.78	.51	.46
.33	.90	.80	.78	.83	.80	.53	.47
.34	.91	.82	.80	.84	.82	.54	.48
.35	.93	.83	.81	.85	.83	.56	.50
.36	.95	.85	.82	.86	.85	.57	.51
.37	.97	.86	.84	.87	.87	.59	.52
.38	.99	.87	.85	.88	.89	.60	.54
.39	26.00	.89	.86	.89	.91	.61	.55
14.40	26.02	20.90	19.88	14.90	26.92	21.63	20.57
.41	.04	.92	.89	.91	.94	.64	.58
.42	.06	.93	.91	.92	.96	.66	.59
.43	.08	.95	.92	.93	.98	.67	.61
.44	.09	.96	.93	.94	27.00	.69	.62
.45	.11	.98	.95	.95	.01	.70	.63
.46	.13	.99	.96	.96	.03	.72	.65
.47	.15	21.01	.97	.97	.05	.73	.66
.48	.17	.02	.99	.98	.07	.74	.68
.49	.18	.03	20.00	.99	.09	.76	.69

Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$	Cl°/oo	S°/oo	σ_0	$\rho_{17.5}$
15.00	27.11	21.77	20.70	15.50	28.01	22.50	21.39
.01	.12	.79	.72	.51	.03	.51	.40
.02	.14	.80	.73	.52	.04	.53	.42
.03	.16	.82	.74	.53	.06	.54	.43
.04	.18	.83	.76	.54	.08	.56	.45
.05	.20	.85	.77	.55	.10	.57	.46
.06	.21	.86	.79	.56	.12	.59	.47
.07	.23	.88	.80	.57	.13	.60	.49
.08	.25	.89	.81	.58	.15	.62	.50
.09	.27	.90	.83	.59	.17	.63	.52
15.10	27.29	21.92	20.84	15.60	28.19	22.64	21.53
.11	.30	.93	.85	.61	.21	.66	.54
.12	.32	.95	.87	.62	.23	.67	.56
.13	.34	.96	.88	.63	.24	.69	.57
.14	.36	.98	.90	.64	.26	.70	.58
.15	.38	.99	.91	.65	.28	.72	.60
.16	.39	22.01	.92	.66	.30	.73	.61
.17	.41	.02	.94	.67	.31	.75	.63
.18	.43	.04	.95	.68	.33	.76	.64
.19	.45	.05	.96	.69	.35	.78	.65
15.20	27.47	22.06	20.98	15.70	28.37	22.79	21.67
.21	.48	.08	.99	.71	.39	.80	.68
.22	.50	.09	21.01	.72	.40	.82	.69
.23	.52	.11	.02	.73	.42	.83	.71
.24	.54	.12	.03	.74	.44	.85	.72
.25	.56	.14	.05	.75	.46	.86	.74
.26	.57	.15	.06	.76	.48	.88	.75
.27	.59	.17	.07	.77	.49	.89	.76
.28	.61	.18	.09	.78	.51	.91	.78
.29	.63	.19	.10	.79	.53	.92	.79
15.30	27.65	22.21	21.12	15.80	28.55	22.93	21.80
.31	.66	.22	.13	.81	.57	.95	.82
.32	.68	.24	.14	.82	.59	.96	.83
.33	.70	.25	.16	.83	.60	.98	.85
.34	.72	.27	.17	.84	.62	.99	.86
.35	.74	.28	.18	.85	.64	23.01	.87
.36	.75	.30	.20	.86	.66	.02	.89
.37	.77	.31	.21	.87	.68	.04	.90
.38	.79	.33	.23	.88	.69	.05	.91
.39	.81	.34	.24	.89	.71	.07	.93
15.40	27.83	22.35	21.25	15.90	28.73	23.08	21.94
.41	.84	.37	.27	.91	.75	.09	.96
.42	.86	.38	.28	.92	.77	.11	.97
.43	.88	.40	.29	.93	.78	.12	.98
.44	.90	.41	.31	.94	.80	.14	22.00
.45	.92	.43	.32	.95	.82	.15	.01
.46	.94	.44	.34	.96	.84	.17	.02
.47	.95	.46	.35	.97	.86	.18	.04
.48	.97	.47	.36	.98	.87	.20	.05
.49	.99	.48	.38	.92	.89	.21	.07

Cl ‰	S ‰	σ_0	$\rho_{17.5}$	Cl ‰	S ‰	σ_0	$\rho_{17.5}$
16.00	28.91	23.22	22.08	16.50	29.81	23.95	22.77
.01	.93	.24	.09	.51	.83	.97	.78
.02	.95	.25	.11	.52	.85	.98	.80
.03	.96	.27	.12	.53	.87	.99	.81
.04	.98	.28	.13	.54	.88	24.01	.82
.05	29.00	.30	.15	.55	.90	.02	.84
.06	.02	.31	.16	.56	.92	.04	.85
.07	.04	.33	.18	.57	.94	.05	.87
.08	.05	.34	.19	.58	.96	.07	.88
.09	.07	.36	.20	.59	.97	.08	.89
16.10	29.09	23.37	22.22	16.60	29.99	24.10	22.91
.11	.11	.38	.23	.61	30.01	.11	.92
.12	.13	.40	.24	.62	.03	.12	.93
.13	.14	.41	.26	.63	.05	.14	.95
.14	.16	.43	.27	.64	.07	.15	.96
.15	.18	.44	.29	.65	.08	.17	.98
.16	.20	.46	.30	.66	.10	.18	.99
.17	.22	.47	.31	.67	.12	.20	23.00
.18	.23	.49	.33	.68	.14	.21	.02
.19	.25	.50	.34	.69	.16	.23	.03
16.20	29.27	23.52	22.35	16.70	30.17	24.24	23.04
.21	.29	.53	.37	.71	.19	.26	.06
.22	.31	.54	.38	.72	.21	.27	.07
.23	.33	.56	.40	.73	.23	.28	.09
.24	.34	.57	.41	.74	.25	.30	.10
.25	.36	.59	.42	.75	.26	.31	.11
.26	.38	.60	.44	.76	.28	.33	.13
.27	.40	.62	.45	.77	.30	.34	.14
.28	.42	.63	.46	.78	.32	.36	.15
.29	.43	.65	.48	.79	.34	.37	.17
16.30	29.45	23.66	22.49	16.80	30.35	24.39	23.18
.31	.47	.67	.51	.81	.37	.40	.20
.32	.49	.69	.52	.82	.39	.42	.21
.33	.51	.70	.53	.83	.41	.43	.22
.34	.52	.72	.55	.84	.43	.44	.24
.35	.54	.73	.56	.85	.44	.46	.25
.36	.56	.75	.57	.86	.46	.47	.26
.37	.58	.76	.59	.87	.48	.49	.28
.38	.60	.78	.60	.88	.50	.50	.29
.39	.61	.79	.62	.89	.52	.52	.31
16.40	29.63	23.81	22.63	16.90	30.53	24.53	23.32
.41	.65	.82	.64	.91	.55	.55	.33
.42	.67	.83	.66	.92	.57	.56	.35
.43	.69	.85	.67	.93	.59	.57	.36
.44	.70	.86	.69	.94	.61	.59	.37
.45	.72	.88	.70	.95	.62	.60	.39
.46	.74	.89	.71	.96	.64	.62	.40
.47	.76	.91	.73	.97	.66	.63	.42
.48	.78	.92	.74	.98	.68	.65	.43
.49	.79	.94	.75	.99	.70	.66	.44

Cl°/oo	S°/oo	σ0	ρ17.5	Cl°/oo	S°/oo	σ0	ρ17.5
17.00	30.72	24.68	23.46	17.50	31.62	25.40	24.15
.01	.73	.69	.47	.51	.64	.42	.16
.02	.75	.71	.48	.52	.65	.43	.17
.03	.77	.72	.50	.53	.67	.45	.19
.04	.79	.73	.51	.54	.69	.46	.20
.05	.81	.75	.53	.55	.71	.47	.22
.06	.82	.76	.54	.56	.73	.49	.23
.07	.84	.78	.55	.57	.74	.50	.24
.08	.86	.79	.57	.58	.76	.52	.26
.09	.88	.81	.58	.59	.78	.53	.27
17.10	30.90	24.82	23.60	17.60	31.80	25.55	24.28
.11	.91	.84	.61	.61	.82	.56	.30
.12	.93	.85	.62	.62	.83	.58	.31
.13	.95	.87	.64	.63	.85	.59	.33
.14	.97	.88	.65	.64	.87	.61	.34
.15	.99	.89	.66	.65	.89	.62	.35
.16	31.00	.91	.68	.66	.91	.64	.37
.17	.02	.92	.69	.67	.92	.65	.38
.18	.04	.94	.71	.68	.94	.66	.40
.19	.06	.95	.72	.69	.96	.68	.41
17.20	31.08	24.97	23.73	17.70	31.98	25.69	24.42
.21	.09	.98	.75	.71	32.00	.71	.44
.22	.11	25.00	.76	.72	.01	.72	.45
.23	.13	.01	.77	.73	.03	.74	.46
.24	.15	.02	.79	.74	.05	.75	.48
.25	.17	.04	.80	.75	.07	.77	.49
.26	.18	.05	.82	.76	.09	.78	.50
.27	.20	.07	.83	.77	.10	.79	.52
.28	.22	.08	.84	.78	.12	.81	.53
.29	.24	.10	.86	.79	.14	.82	.55
17.30	31.26	25.11	23.87	17.80	32.16	25.84	24.56
.31	.27	.13	.88	.81	.18	.85	.57
.32	.29	.14	.90	.82	.20	.87	.59
.33	.31	.16	.91	.83	.21	.88	.60
.34	.33	.17	.92	.84	.23	.90	.62
.35	.35	.18	.94	.85	.25	.91	.63
.36	.36	.20	.95	.86	.27	.93	.64
.37	.38	.21	.97	.87	.29	.94	.66
.38	.40	.23	.98	.88	.30	.95	.67
.39	.42	.24	.99	.89	.32	.97	.69
17.40	31.44	25.26	24.01	17.90	32.34	25.98	24.70
.41	.46	.27	.02	.91	.36	26.00	.71
.42	.47	.29	.04	.92	.38	.01	.73
.43	.49	.30	.05	.93	.39	.03	.74
.44	.51	.32	.06	.94	.41	.04	.75
.45	.53	.33	.08	.95	.43	.06	.77
.46	.55	.34	.09	.96	.45	.07	.78
.47	.56	.36	.11	.97	.47	.09	.80
.48	.58	.37	.12	.98	.48	.10	.81
.49	.60	.39	.13	.99	.50	.11	.82

Cl‰	S‰	σ_0	$\rho_{17.5}$	Cl‰	S‰	σ_0	$\rho_{17.5}$
18.00	32.52	26.13	24.84	18.50	33.42	26.86	25.53
.01	.54	.14	.85	.51	.44	.87	.54
.02	.56	.16	.86	.52	.46	.88	.55
.03	.57	.17	.88	.53	.48	.90	.57
.04	.59	.19	.89	.54	.49	.91	.58
.05	.61	.20	.91	.55	.51	.93	.60
.06	.63	.22	.92	.56	.53	.94	.61
.07	.65	.23	.93	.57	.55	.96	.62
.08	.66	.24	.95	.58	.57	.97	.64
.09	.68	.26	.96	.59	.58	.99	.65
18.10	32.70	26.27	24.97	18.60	33.60	27.00	25.66
.11	.72	.29	.99	.61	.62	.02	.68
.12	.74	.30	25.00	.62	.64	.03	.69
.13	.75	.32	.02	.63	.66	.04	.71
.14	.77	.33	.03	.64	.68	.06	.72
.15	.79	.35	.04	.65	.69	.07	.63
.16	.81	.36	.06	.66	.71	.09	.75
.17	.83	.38	.07	.67	.73	.10	.76
.18	.84	.39	.08	.68	.75	.12	.78
.19	.86	.40	.10	.69	.77	.13	.79
18.20	32.88	26.42	25.11	18.70	33.78	27.15	25.80
.21	.90	.43	.13	.71	.80	.16	.82
.22	.92	.45	.14	.72	.82	.18	.83
.23	.94	.46	.15	.73	.84	.19	.84
.24	.95	.48	.17	.74	.86	.20	.86
.25	.97	.49	.18	.75	.87	.22	.87
.26	.99	.51	.20	.76	.89	.23	.89
.27	33.01	.52	.21	.77	.91	.25	.90
.28	.03	.54	.22	.78	.93	.26	.91
.29	.04	.55	.24	.79	.95	.28	.93
18.30	33.06	26.56	25.25	18.80	33.96	27.29	25.94
.31	.08	.58	.26	.81	.98	.31	.95
.32	.10	.59	.28	.82	34.00	.32	.97
.33	.12	.61	.29	.83	.02	.34	.98
.34	.13	.62	.31	.84	.04	.35	26.00
.35	.15	.64	.32	.85	.05	.36	.01
.36	.17	.65	.33	.86	.07	.38	.02
.37	.19	.67	.35	.87	.09	.39	.04
.38	.21	.68	.36	.88	.11	.41	.05
.39	.22	.70	.37	.89	.13	.42	.07
18.40	33.24	26.71	25.39	18.90	34.14	27.44	26.08
.41	.26	.72	.40	.91	.16	.45	.09
.42	.28	.74	.42	.92	.18	.47	.11
.43	.30	.75	.43	.93	.20	.48	.12
.44	.31	.77	.44	.94	.22	.49	.13
.45	.33	.78	.46	.95	.23	.51	.15
.46	.35	.80	.47	.96	.25	.52	.16
.47	.37	.81	.49	.97	.27	.54	.18
.48	.39	.83	.50	.98	.29	.55	.19
.49	.40	.84	.51	.99	.31	.57	.20

Cl°/oo	S°/oo	0°	17,5	Cl°/oo	S°/oo	0°	17,5
19.00	34.33	27.58	26.22	19.50	35.23	28.31	26.91
.01	.34	.60	.23	.51	.25	.32	.92
.02	.36	.61	.24	.52	.26	.34	.94
.03	.38	.63	.26	.53	.28	.35	.95
.04	.40	.64	.27	.54	.30	.37	.96
.05	.42	.66	.29	.55	.32	.38	.98
.06	.43	.67	.30	.56	.34	.40	.99
.07	.45	.68	.31	.57	.35	.41	27.01
.08	.47	.70	.33	.58	.37	.43	.02
.09	.49	.71	.34	.59	.39	.44	.03
19.10	34.51	27.73	26.36	19.60	35.41	28.46	27.05
.11	.52	.74	.37	.61	.43	.47	.06
.12	.54	.76	.38	.62	.44	.48	.07
.13	.56	.77	.40	.63	.46	.50	.09
.14	.58	.79	.41	.64	.48	.51	.10
.15	.60	.80	.42	.65	.50	.53	.12
.16	.61	.82	.44	.66	.52	.54	.13
.17	.63	.83	.45	.67	.53	.56	.14
.18	.65	.84	.47	.68	.55	.57	.16
.19	.67	.86	.48	.69	.57	.59	.17
19.20	34.69	27.87	26.49	19.70	35.59	28.60	27.19
.21	.70	.89	.51	.71	.61	.62	.20
.22	.72	.90	.52	.72	.62	.63	.21
.23	.74	.92	.54	.73	.64	.64	.23
.24	.76	.93	.55	.74	.66	.66	.24
.25	.78	.95	.56	.75	.68	.67	.25
.26	.79	.96	.58	.76	.70	.69	.27
.27	.81	.98	.59	.77	.71	.70	.28
.28	.83	.99	.60	.78	.73	.72	.30
.29	.85	28.00	.62	.79	.75	.73	.31
19.30	34.87	28.02	26.63	19.80	35.77	28.75	27.32
.31	.88	.03	.65	.81	.79	.76	.34
.32	.90	.05	.66	.82	.81	.78	.35
.33	.92	.06	.67	.83	.82	.79	.36
.34	.94	.08	.69	.84	.84	.80	.38
.35	.96	.09	.70	.85	.86	.82	.39
.36	.97	.11	.72	.86	.88	.83	.41
.37	.99	.12	.73	.87	.90	.85	.42
.38	35.01	.14	.74	.88	.91	.86	.43
.39	.03	.15	.76	.89	.93	.88	.45
19.40	35.05	28.16	26.77	19.90	35.95	28.89	27.46
.41	.07	.18	.78	.91	.97	.91	.48
.42	.08	.19	.80	.92	.99	.92	.49
.43	.10	.21	.81	.93	36.00	.94	.50
.44	.12	.22	.83	.94	.02	.95	.52
.45	.14	.24	.84	.95	.04	.96	.53
.46	.16	.25	.85	.96	.06	.98	.54
.47	.17	.27	.87	.97	.08	.99	.56
.48	.19	.28	.88	.98	.09	29.01	.57
.49	.21	.30	.90	.99	.11	.02	.59

DETERMINATION OF DISSOLVED OXYGEN IN FRESH AND SEA WATER

Notes Prepared by M.J. Hollister (4)

ABSTRACT

Dissolved oxygen in fresh or sea water is determined by Winkler's method (Winkler, 1888; Jacobsen and Knudsen, 1921; American Public Health Association, 1946). The macro procedure and apparatus are based on a sample of approximately 250 ml. of water, but may be applied to samples from 50 to 500 ml. by suitable adjustments of the size of the apparatus and quantities of reagents. No adjustment of the concentration of reagents is required. A portable analysis unit for use in the field is illustrated (figure 3).

INTRODUCTION

The Winkler method as described is used for determining dissolved oxygen in fresh or salt water in the absence of reducing or oxidizing substances such as nitrites, ferric and ferrous salts, sulphites, thiosulphates, polythionates, free chlorine, hypochlorites and organic material that might occur in domestic and industrial sewage, and chlorinated wastes. These interfering substances may introduce considerable errors if they are in excess. Modifications to overcome these interfering substances are described by the American Public Health Association (1946) and Ellis, Westfall and Ellis (1946). The latter reference describes procedures to determine what modifications are required in the presence of a number of interfering substances and gives a detailed discussion of dissolved oxygen determinations in fresh water. Thompson and Robinson (1939) describe important modifications in the Winkler method when used to determine dissolved oxygen in sea water, explaining the complex chemical reactions involved in the method.

REACTIONS

The Winkler method requires that a sample of water be treated with an alkaline manganous solution while protected from oxygenation by air. A flocculent white precipitate of manganous hydroxide forms at first (Treadwell and Hall, 1937).

$$Mn^{++} + 2OH^{-} \rightarrow Mn(OH)_2$$

which rapidly becomes brown in the presence of the dissolved oxygen owing to the formation of manganous manganites which are less soluble than $Mn(OH)_2$.

A part of the manganous hydroxide is oxidized slowly to manganous acid.

$$2\ Mn(OH)_2 + O_2 \rightleftharpoons 2\ H_2MnO_3$$

which on coming in contact with basic manganous hydroxide, immediately forms a manganite salt.

$$H_2MnO_3 + Mn(OH)_2 \rightleftharpoons MnMnO_3 + 2\ H_2O$$

or possibly

$$2\ H_2MnO_3 + Mn(OH)_2 \rightleftharpoons MnH_2(MnO_3)_2 + 2\ H_2O$$

When acidified to excess in the presence of an iodide the iodine is released quantitatively. This may be regarded as a reaction of the manganite.

$$2\ H_2MnO_3 + 2I^- + 8\ H^+ \rightarrow 2\ Mn^{++} + I_2 + 6\ H_2O$$

Then the iodine solution is titrated with standard sodium thiosulphate solution.

$$2\ Na_2S_2O_3 + I_2 \rightarrow 2\ NaI + Na_2S_4O_6$$

[redacted]

Reagent 1. Manganous solution

Dissolve 480 g. of manganous sulphate ($MnSO_4 \cdot 4H_2O$)
or 400 g. of $MnSO_4 \cdot 2\ H_2O$
or 420 g. of $MnCl_2 \cdot 4\ H_2O$
in distilled water and make up to one liter.

It is necessary that iron impurities do not exceed 0.001% and that manganic and ferric salts be absent. If these are absent the solution will not liberate more than a trace of iodine when added to an acidified solution of potassium iodide.

Reagent 2. Alkaline iodide solution

Dissolve 500 g. of sodium hydroxide (NaOH)

or 700 g. of potassium hydroxide (KOH)

in 500 ml. of distilled water.

Dissolve 135 g. of sodium iodide (NaI)
or 150 g. of potassium iodide (KI)
in 200 ml. of distilled water.

Add the latter to the former and make up to one liter with distilled water.

It is permissable to use good commercial grades of sodium hydroxide (lye) and potassium iodide if the absence of peroxide and periodate impurities is ensured.

Test for Oxidising Impurities

Test 1.

Add one ml. each of reagents one and two to a glass stoppered bottle which has previously been filled to overflowing with water. Stopper, agitate, and allow the precipitate to settle for at least 30 minutes, or better, centrifuge to solidify the precipitate. The supernatant solution contains no dissolved oxygen but will contain peroxides or periodates if they occur as impurities in the reagents.

Very carefully siphon the supernatant solution into a second smaller glass stoppered bottle, filling it to overflowing. It is important that none of the precipitate be transferred over to the smaller bottle. Add reagents 1 and 2, below the surface of the solution, and quickly stopper the bottle and mix. Add 2 ml. of 36 N sulphuric acid, stopper and mix. Test for free iodine with starch indicator. If the test is negative the reagents are satisfactory. If the test is positive a blank titer value based on the sample volume should be determined.

Test 2.

Dilute one ml. of reagent 2 to 10 ml. with distilled water, acidify with 3 ml. of 5 N sulphuric acid and test for free iodine with starch solution. Blue color indicates oxidising impurities present, wherefore a blank titer value should be determined as outlined in test 1.

Reagent 3. Sulphuric acid (36 N)

Concentrated sulphuric acid of specific gravity 1.83 to 1.84 is approximately 36 Normal.

The electrolytic grade of acid is satisfactory if it does not release iodine from potassium iodide.

Test of sulphuric acid

Add one drop of the acid to a solution of one gram of potassium iodide (iodate free) in 10 ml. of distilled water, and add a few drops of starch solution. If there is no blue color developed immediately the acid is satisfactory.

Reagent 4. Sodium thiosulphate solution (0.01 N)

Dissolve 2.5 grams of sodium thiosulphate ($Na_2S_2O_3.5\ H_2O$) in one liter of water, and age for several days.

The normality will remain constant for several months if one drop of carbon disulphide per liter is added and the solution is protected from air-borne carbon dioxide by a sodium hydroxide air trap (cf. APPARATUS and figure 1).

It is customary to prepare a stock solution of reagent 4 in an 18 liter (5 gallon) carboy, and withdraw and standardize portions as required for current use.

Reagent 5. Starch solution

A starch solution which will not deteriorate over a 12 month period was described by Platner (1941).

Prepare a suspension of 2 grams of powdered starch in 300 to 400 ml. of water. Add a 20% solution of sodium or potassium hydroxide, or the solid caustic, with stirring, until a thick, syrupy, almost clear solution is obtained. Allow the solution to stand for about one hour to ensure complete action by the alkali. Using litmus paper as an indicator, add concentrated hydrochloric acid until the solution is neutral, or slightly acid. Add one ml. of glacial acetic acid as a preservative.

The starch solution is satisfactory if it turns a bright blue when one ml. is added to a faintly straw-colored iodine solution. If the solution turns purple, discard the starch solution.

APPARATUS

1. Sample Bottles

Provide chemically clean glass-stoppered bottles of 250 to 300 ml. capacity. The best type are Biochemical Oxygen Demand bottles which have the end of the glass stopper beveled, so that no air is trapped when it is inserted in a completely filled bottle.

2. Reagent bottles

Reagents 1, 2, 3, and 5 are normally carried in stout glass bottles of about 200 ml. capacity (figure 2). Separate pipettes are required for each reagent. It is convenient to fit a dropping pipette through the rubber stopper as shown in figure 2. Filling and delivery of the poisonous solutions is controlled by a rubber bulb.

3. Measuring - titration flask

A standard volume of the sample to be titrated is measured in a flask fitted as shown in figure 3. A 250 ml. Erlenmeyer flask is fitted with a suspension arrangement which allows it to swing freely from a hook. A small bore (3 mm.) glass siphon is provided which leaves a suitable volume (about 125 ml.) for titration in the flask. The position for the siphon is marked by a filed notch on the lip and the bulge of the flask.

The whole contents of the sample bottle, after treatment with the three reagents, are poured into the measuring flask. The siphon is placed in position and if the flask is full it will prime itself. The flask is hung from a hook so that it may swing freely and the siphon allowed to run until it stops. The volume remaining in the flask is titrated.

The flask is calibrated by averaging five weighings of the volume remaining after siphoning from the hanging position. These weights should be constant within 0.5%, and are expressed as residual volume at 20°C.

The addition of reagents 1, 2, and 3 displaces 3 ml. of water from the sample bottle. The "volume titrated" is arbitrarily taken to be 1.5 ml. (or corresponding value) less than the residual volume of the flask. The maximum error due to this procedure is less than 0.5%.

4. Basic Titration assembly

The burette, bottle of reagent 4, and carbon dioxide trap are connected similarily to a Squibb type burette as shown in figure 1. Air pressure is generated by pumping the rubber bulb while the air vent is closed. Air is filtered through the trap which increases the pressure in the bottle forcing the thiosulphate solution through the supply tube to the burette. When the burette is filled above the outlet of the delivery tip, pumping is stopped and the air vent is opened, then the excess solution in the burette siphons back to the solution bottle. The delivery tip is adjusted to leave the burette full to the zero mark. A slot cut in the side of the cork holding the delivery tip provides a channel for air flow out the top of the burette.

5. Portable laboratory

Frequently it is necessary to make oxygen determinations away from a base laboratory and it was found convenient to assemble all the necessary apparatus in a portable kit.

In this unit the titration equipment (figure 1) is fixed in position and storage compartments are provided for the reagents, measuring flasks, spare items, etc. An electric lamp is fitted to illuminate the measuring flask during the titration. The sampling bottles are packed in a separate case.

PROCEDURE

1. Sampling

The sample should be taken in a manner that will ensure at least threefold displacement of the water in the sample bottle, without entrainment of air bubbles.

If the sample is to be taken from a tap, a rubber hose that will reach the bottom of the sample bottle should be fitted. The bottle should be allowed to fill with the free end of the tubing under the water surface, and should overflow sufficiently to displace any water that might have been aerated.

If the sample is to be taken beneath a water surface the bottle should be filled by a suction arrangement as shown in figure 2.

Stopper the bottle as soon as it is filled.

2. Adding the reagents

Within 10 minutes of the collection of the sample introduce measured quantitites of reagent 1, then reagent 2, below the surface of the water in the bottle by means of a separate dropping pipette for each reagent. Re-stopper the sample bottles immediately and mix the contents thoroughly by holding the bottle neck with the thumb and first two fingers and twirling it with a rolling wrist motion.

The quantity of reagents added depends upon the volume of the sample bottles.

Volume of Sample bottle (ml.)	Volume of reagents required (ml.)
75 - 125	0.5
125 - 250	1.0
250 - 400	1.5

A flocculent precipitate forms during the reaction, probably manganous and manganic hydroxide which varies from white to brown depending upon the amount of dissolved oxygen present. When this precipitate has settled about half way down the bottle introduce the measured volume of reagent 3 below the surface of the sample by means of the dropping pipette. Re-stopper and agitate the sample.

A brown solution of the iodine is obtained, which may contain particles of precipitate if the oxygen content is high (vicinity of 10 ppm.). This precipitate will generally turn black in a few minutes, and may dissolve on standing, in which case it may be disregarded. If it remains a light brown color a further 0.5 ml. of reagent 3 should be added, and the sample reagitated. Any remaining precipitate may be disregarded.

3. Titration

Within one hour of adding reagent 3, agitate the sample and empty the whole into the measuring flask. Suspend the flask from a hook so that it may be swung freely, adjust the siphon, and allow it to run until it stops.

Titrate the aliquot remaining in the measuring flask with reagent 4 (standard sodium thiosulphate solution) over a white surface, until the pale straw color of iodine has almost vanished. Add one ml. of reagent 5 (starch solution) whereupon the solution turns blue. Titrate to the end point at which the blue color vanishes.

The titration is sensitive to the nearest half drop (± 0.02 ml.) which implies a probable error of 0.1% which is within the limits of error of other steps in the procedure. Read the burette to the nearest 0.02 ml.

The titer, and sensitivity of the end point vary with temperature, and this titration should always be made at a temperature corresponding to that of standardization (20°C ± 2°) and with the same starch solution.

At low temperatures (10°C and less) the blue color may reappear on standing a few seconds, but this should be disregarded.

STANDARDIZATION

1. Standardization with Iodine

Provide a small glass stoppered weighing bottle (5 ml.) containing 0.1 to 0.2 grams of potassium iodide in one to two ml. of distilled water. Weigh accurately.

Quickly transfer about 0.01 grams of resublimed iodine to the weighing bottle, re-stopper, and weigh again. The difference from the first weighing is the weight of iodine taken.

Transfer the stoppered weighing bottle to a 250 ml. Erlenmeyer flask containing about 150 ml. of distilled water, and open the bottle under water (Bradstreet, 1944).

Titrate the iodine solution with sodium thiosulphate solution (reagent 4) as instructed under PROCEDURE - titration. Successive standardizations should check to 0.2 % (± 0.04 ml.).

$$\text{Normality} = \frac{\text{wt. of iodine}}{\text{titer(ml.)}} \times 7.879 \qquad \text{......(1)}$$

Iodine produces a blue color with starch only when hydriodic acid or a soluble iodide is present, and further formation of the blue color is largely influenced by the concentration of the iodide solution. Therefore the concentration of the iodide should be the same in the standardization as in the analyses (Treadwell and Hall, 1919).

2. Standardization with Potassium iodide-iodate solution

Prepare an 0.02 N solution of $KI - KIO_3$ by dissolving

10 g. potassium iodide (KI)
0.72 g. potassium iodate (KIO_3)
0.1 g. sodium hydroxide (NaOH)

in distilled water and make up to one liter.

The solution must be clear and colorless, otherwise it must be discarded.

The normality and iodine content are determined by titration with standard sodium thiosulphate solution.

Accurately transfer 10 ml. of the $KI - KIO_3$ solution to a 350 ml. Erlenmeyer flask containing 125 ml. of distilled water. Acidify with 2 ml. of reagent 3 and titrate to a starch end point with standard sodium thiosulphate solution.

$$\underset{(KI-KIO_3)}{\text{Normality}} = \frac{\text{(N of thiosulphate sol'n) x (ml. of titer)}}{\text{(ml. of sample)}} \quad \text{....(2)}$$

A stock solution of $KI - KIO_3$ kept in a rubber stoppered brown glass bottle varied only 0.0004 N during 2 years while three-quarters of the solution was used.

More detailed discussions of the methods of standardization are given by Bradstreet (1944), Scott (1925), Treadwell and Hall (1919), and Thompson and Robinson (1939).

CALCULATIONS

1. Concentration

The concentration of dissolved oxygen may be expressed as milligrams per liter by:

$$\text{Mg. } O_2/l = \frac{\text{8000 x (Titer) x (N of thiosulphate)}}{\text{(Volume of sample titrated)}} \quad \text{....(3)}$$

The concentration may also be expressed as milligrams per kilo or parts per million (p.p.m.) by introducing the density of the water, which has been ascertained independently.

$$\underset{\text{(p.p.m.)}}{\text{Mg. O}_2\text{/kilo}} = \frac{8000 \times (\text{Titer}) \times (\text{N of thiosulphate})}{(\text{Vol. of sample titrated}) \times (\text{density of water})} \quad ....(4)$$

The difference between the values obtained in equations 3 and 4 seldom exceeds 3%.

The concentration may be expressed as milligram-atoms by multiplying the above equations by 0.0625 (Tully, 1938).

2. Volume

The volume of the dissolved gas (cc. per liter or cc. per kilo) is obtained by dividing the value obtained in equation 3 or 4 by the weight of one cc. of oxygen at the water temperature (T°C) and the barometric pressure (P mm of mercury) at the time of the collection of the water sample. This weight may be evaluated with sufficient accuracy from:

$$\text{Wt. of one cc. of oxygen} = 0.001429 \times \frac{273}{273 + T^\circ C} \times \frac{760}{P}$$

$$= \frac{296.47}{(273 + T^\circ C) \times P} \quad ....(5)$$

3. Saturation

It is frequently desirable to express the concentration as the degree of saturation, or proportion of solubility.

$$\frac{\text{Degree of saturation}}{\text{of dissolved oxygen}} \;\; = \frac{\text{Observed concentration}}{\text{Solubility}} \quad ....(6)$$

The observed concentration of dissolved oxygen is expressed by equation 3 (mg./l) or equation 4 (mg./kilo). The solubility of oxygen in sea water saturated with moist air at 760 mm. atmospheric pressure, as a function of temperature and salinity is given in the tables of Whipple and Whipple (1911). The relation is conveniently expressed in the appended nomograph (Tully, 1942).

[illegible]

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COMPARISON METHOD FOR DISSOLVED OXYGEN (8)

Where precise results are not required it is practical to compare the intensity of color of the iodine solution with known standards, in Nessler tubes, photometer, or Lamotte type comparator (cf. section on colorimetric pH).

A convenient comparator series may be prepared by filling suitable tubes with standard iodine solutions, and sealing them off.

Apparatus

Water sample bottles and dropper bottles for reagents 1, 2, and 3 as described above.

Comparator block as shown in figure 4 similar to Lamotte pH comparator.

Pyrex comparator tubes as shown.

Partially closed pyrex comparator tubes as shown.

Reagents

Reagents 1, 2, and 3 as described above.

Prepare and standardize an approximately 0.000938 N iodine solution. Accurately weigh about 119 mg. resublimed iodine in a weighing bottle containing one gram of pure potassium iodide, and a minute crystal of sodium or potassium hydroxide. Release under water, and make up accurately to one liter in distilled water.

Dilute successive portions to prepare equivalent standards accordind to Table I. It is practical to prepare standards at intervals corresponding to 0.5 mg/l dissolved oxygen.

Fill the prepared (and cleaned) comparator tubes with freshly prepared iodine solution and seal off with fine flame of the blow torch. Label tubes with their equivalent oxygen concentration.

Procedure

Collect and treat the water sample with reagents 1, 2, and 3 as previously outlined. Fill one comparator tube with the iodine solution from the sample, and two other tubes with the natural water. View as indicated in figure 4. Bracket the sample between two of the standards, and estimate the oxygen concentration as equal to one, or half way between the standards.

Table I

Equivalent Concentration of Dissolved oxygen mg/1	Concentration of iodine solution mg/1	Normality of iodine solution
15	119.0	9.38×10^{-4}
14	111.0	8.25
13	109.1	8.12
12	95.1	5.94
11	87.2	6.87
10	79.2	6.25
9	71.3	5.62
8	63.4	5.00
7	55.5	4.37
6	47.5	3.75
5	39.8	3.125
4	31.7	2.500
3	23.8	1.874
2	15.86	1.250
1	7.92	0.625

NOTES

1. The iodine solution will not keep, and therefore must be fresh when the tubes are filled.

2. The iodine solution must not be heated when the tubes are being filled.

3. If the iodine solution is neutral or acid, free iodine will be released from the potassium iodide on exposure to light. If it is significantly basic, the iodine will form the iodide. The solution should be between pH 8.0 - 9.0.

4. Alkalis contained in soft glass are moderately soluble and will react with the iodine to form iodides in basic solutions. Therefore pyrex comparator tubes should be used.

5. The standards should be kept cool, and stored in the dark. They should be checked against known standards at bi-weekly intervals, and be renewed every six months or there abouts.

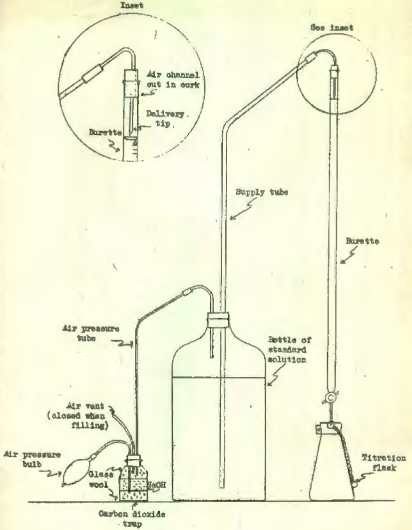

Figure 1. Squibb type burette assembly, for dissolved oxygen determination by Winkler method.

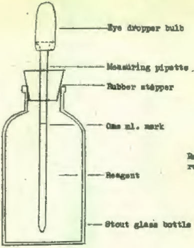

Figure 2

Reagent bottles for reagents 1, 2, 3, and 5.

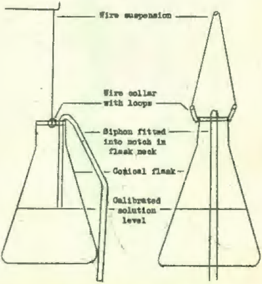

Figure 3. Measuring-titration flask

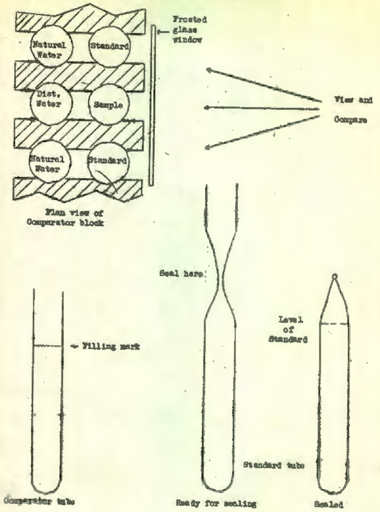

Figure 4. Comparator Equipment.

DETERMINATION OF HYDROGEN-ION CONCENTRATION (1,2)

Water Ionization Constant

Conductivity experiments indicate that water acts as a very weak binary electrolyte, dissociating into H^+ and OH^- according to

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1)$$

Then according to the law of homogeneous equilibrium

$$\frac{(H^+)\ (OH^-)}{(H_2O)} = 1.57 \times 10^{-14} \qquad (2)$$

where (H^+), (OH^-) and (H_2O) represent ionic or molar concentrations per liter and K is the equilibrium constant. By conductivity measurements, the concentrations of (H^+) and (OH^-) have been found to be 0.93×10^{-7} mols per liter in neutral water at 20°C. This extremely small ionization leaves the (H_2O) unchanged and a constant for all practical purposes, so equation (2) becomes

$$(H^+)\ (OH^-) = K(H_2O) = K_w \qquad (3)$$

K_w is known as the water ionization constant. Substituting the value 0.93×10^{-7} for (H^+) and (OH^-), the value of K_w becomes 0.86×10^{-14} at 20°C. At higher temperatures there is increased ionization of water and at lower temperatures less ionization, so the value of K_w varies with temperature.

Variation of K_w with Temperature

Temperature (°C.)	K_w
0	0.08×10^{-14}
15	0.46
20	0.86
25	1.2
30	1.5

pH

At neutrality, the concentration of the hydrogen-ion is equal to that of the hydroxyl-ion. Now if an acid is added, the (H^+) is increased, consequently the (OH^-) must be decreased proportionately for their product is equal to a constant for any given temperature. And vice versa if the (OH^-) is increased, the (H^+) must of necessity be decreased accordingly.

It is inconvenient to be constantly writing the concentration of H^+ with such large numbers as 0.93×10^{-7} or 0.000,000,093 mols per liter. The term pH has been offered as a more convenient and workable form. pH is defined as (1) the negative logarithm of the hydrogen-ion concentration in mols per liter, or (2) the logarithm of the reciprocal of the hydrogen-ion concentration in mols per liter.

That is,

$$pH = \log \frac{1}{(H^+)} \qquad (4)$$

The pH of neutral water at 20°C. is 7 since the (H^+) is normally considered to be 10^{-7}. As a second example, if the (H^+) is 10^{-4}, the pH is 4. The pH of water at temperatures other than 20°C., though obviously still neutral, is not 7. It has a different (H^+) because of the different degrees of ionization of water at various temperatures.

Variation of pH of Water with Temperature

Temperature (°C)	pH
0	7.55
15	7.10
25	6.90
30	6.85
40	6.71

Buffers

Certain substances are known which, within certain limits, tend to resist the normal change of hydrogen-ion concentration following the addition of an acid or a base. These substances are called buffers. Buffering action is explained as follows:

A buffer is composed of a solution of either a salt of a strong base and a weak acid and the weak acid, or a salt of a weak base and strong acid and the weak base. Sodium acetate acid may be used as an example of the former type and ammonium chloride and ammonium hydroxide of the latter.

For example, in a solution of sodium acetate and acetic acid, there are the following equilibria:

$$HAc \rightleftharpoons H^+ + Ac^- \qquad (5)$$

$$NaAc \rightarrow Na^+ + Ac^- \qquad (6)$$

Since acetic acid is a weak acid, only a small proportion ionizes. On the other hand, most of the sodium acetate exists in the ionic form.

Now if an acid is added to this solution, the hydrogen-ion of the added acid immediately combines with the acetate-ion leaving the hydrogen-ion concentration practically the same as in the original buffer solution. This must necessarily follow as:

$$\frac{(H^+)\ (Ac^-)}{(HAc)} = K \qquad (7)$$

and as the large acetate-ion concentration remains practically unchanged upon the addition of small amounts of hydrogen-ion. Therefore the hydrogen-ion concentration must also remain unchanged for equation (7) to apply.

However, if a base is added the OH^- of the added base combines with the H^+ from the acetic acid. Just as soon as the existing hydrogen-ions are removed, the equilibrium, as shown by equation (5), becomes unbalanced. More acetic acid then ionizes to replace the hydrogen-ions now neutralized, until equilibrium is re-established again at practically the original (H^+).

By varying the relative proportions of sodium acetate and acetic acid, solutions of any desired pH within certain limits, may be prepared, since the law of homogeneous equilibrium must still apply even with this mixture (see equation 7). Even through the (Ac^-) may be varied by the addition of sodium acetate, the (HAc) remains practically constant; obviously then the (H^+) must vary inversely as the (Ac^-). Standard buffer solutions of a definite pH are prepared from mixtures of these compounds or others of a similar type. Such solutions are more stable over long periods of time than solutions containing small amounts of acids or bases which might be very easily changed by absorption of carbon dioxide from the air or by alkali from the glass container, or even by the added H or OH^- from the ionization of the indicator.

Indicators

One of the most common methods of determination of pH is to add to the unknown solution an appropriate indicator and match the resulting color with buffer solutions of known pH value containing the same indicator. The indicators so selected for this purpose are for the most part weak organic acids and bases which are able to exist in two forms possessing different colors. Being weak acids or bases, the law of homogeneous equilibrium applies to them just as it does to any other weak acid or base. The equilibrium may be indicated by the following equations:

$$HIn' \rightleftharpoons HIn \rightleftharpoons H^+ + In^- \qquad (8)$$

$$\frac{(H^+)\ (In^-)}{(HIn')} = K \qquad (9)$$

The two colored forms are the HIn' molecule and the In-ion. The color of the indicator is determined by the ratio of these two forms; i.e. (In)/(HIn'). Since this ratio multiplied by the (H^+) is equal to a constant, the ratio and therefore the color of the indicator itself is dependent upon the (H^+).

It has been found that there is no further visible color change when the ratio of $(In^-)/(HIn')$ becomes greater than approximately 91/9 or less than 9/91. That is, the visible color change occurs within a hundred-fold change in the concentration of either the (In^-) or (HIn'). Therefore there must be a corresponding hundred-fold change in the (H^+). The usable color range, then, of indicators in general corresponds to a range of 2 pH units. Although the range of any one indicator is thus limited, fortunately there is sufficient variation in the pH of the ranges of the numerous indicators so that any hydrogen-concentration may be determined by the proper selection of indicators.

pH Range of Indicators

Indicator	pH
Thymol Blue	1.2 - 2.8
Brom Phenol Blue	3.0 - 4.6
Methyl Red	4.4 - 6.0
Brom Cresol Purple	5.2 - 6.8
Brom Thymol Blue	6.0 - 7.6
Cresol Red	7.2 - 8.8
Thymol Blue	8.0 - 9.6

pH with the Double Wedge Comparator

The double wedge comparator consists of a rectangular glass cell with a glass partition running diagonally across, thus dividing it into two wedge shaped cells. One compartment is filled with an acid solution containing 0.5 ml. of 0.04% indicator per 10 ml. of solution, while the other compartment is filled with an alkaline solution with the same indicator concentration. The cell is then closed with a suitable lid to prevent evaporation or the absorption of carbon dioxide from the air. Viewing the cell laterally, at one end the acid color of the indicator is only observed while at the other end only the alkaline color is seen. In between are all the intermediate mixtures of the two colors. The cell is calibrated (1) and a scale prepared on the side graduated into divisions of 0.02 pH units.

For a determination the unknown sample, taken immediately after sampling (2) is mixed with a 0.04% indicator solution (3) in the proportion of 0.5 ml. of indicator per 10 ml. of solution. The solution is transferred to a small cell made to slide along on top of the double wedge comparator. The construction of the cell is such that its internal width is the same as the sum of the internal widths of the two wedges at any one position. This insures the same thickness of solution and the same intensity of indicator color in the two cells. After the color of the unknown in the sliding cell has been matched with some portion of the double wedge, the pH is read directly from the scale (4).

pH Determination with the Hellige Comparator (5)

Immediately after collection of the water sample (2), rinse one of the graduated 10 ml. test tubes and then fill to the mark. Add 0.5 ml. (6) of indicator (3). Thoroughly mix (7) the indicator with the solution. Place the tube in the compartment of the comparator nearest the source of light. Compare with the various colored glasses of the standard color disc (8). The individual glasses differ by 0.2 pH units. By careful interpolation, an accuracy of ±0.05 pH is attained in the matching by this method. The observed pH should be corrected for temperature and salt effect (4).

Notes

1. The cell should be calibrated colorimetrically at 20°C. against standard buffer solutions which have been checked against the hydrogen-electrode.

2. Although the wedge comparator, the La Motte standard buffers and the Hellige color discs are calibrated for use with water samples at 20°C., a correction can be applied (as will be seen later) if the temperature of the water differs materially. Since it is advisable to determine the pH immediately after collection as loss or absorption of carbon dioxide takes place on standing with resulting change in pH, the temperature of the water samples is usually less than that of the standards.

3. The pH of sea water is usually within the range of cresol red.

4. As will be explained more fully later, it is necessary to apply a correction for the effect of dissolved salts and temperature.

5. The Hellige color discs and comparator are more convenient to use than the La Motte comparator block with standard buffers. The light attachment of the Hellige comparator increases the accuracy of the color matching considerably. Neither of these comparators permits the accuracy that may be attained with the double wedge comparator.

6. This same amount of indicator was used in the preparation of the color tubes of La Motte and in the calibration of the color disc of the Hellige comparator.

7. The mixing is best done by grasping the upper end of the test tube between the ends of the two first fingers and thumb and then whirling, centrifuging the contents of the tube.

8. The color of the standard buffer tubes gradually fades. After a period of about a year, they should be replaced.

Correction pH

Salt Error

The presence of dissolved electrolytes is known to increase the ionization of weak acids and bases. This applies to indicators, which are either weak acids or bases, as well as it does to other weak acids or bases. In other words, the dissolved salts in sea water affect the dissociation of the indicator to such an extent that the apparent pH is in error if it has been determined by matching with buffer solutions or with a wedge comparator solution of different salt content. The salt effect correction at various chlorinities has been determined by Ramage and Miller, J. Am. Chem. Soc. 47 1230 (1925).

Salt Effect Corrections

Chlorinity	Correction	Chlorinity	Correction
1		11	-0.24
2		12	.24
3	-0.12	13	.25
4	.14	14	.25
5	.16	15	.26
6	.18	16	.26
7	.20	17	.27
8	.21	18	.27
9	.22	19	.27
10	.23		

Temperature

Temperature has been shown to play a complex role in the accurate determination of pH. Usually the temperature of the water sample in situ is considerably different from that of the reference standard. It is the pH in situ which is of interest yet, with this temperature difference, two errors may result in the pH measurements. First, the dissociation constant of the indicator is different at the two temperatures, thus giving different colors for the same pH. This may be corrected by applying the following equation:

$$pH_w = pH_{t_b} + a(t_b - t_w)$$

where

pH_w is the pH of the water in situ.
pH_{t_b} is the pH of the comparison standard.
a is a constant indicating how much the dissociation exponent of the indicator varies for a temperature change of one degree. For cresol red in a solution of chlorinity of $19^{oo}/_{oo}$, it is 0.0053.
t_b is the temperature of the comparison standard.
t_w is the temperature of the water in situ.

Second, if the temperature of the sample is several degrees higher at the time of measurement than at collection, the previous equation must be modified by adding the further correction.

$$B(t_w' - t_w)$$

where

B is a constant typical of the indicator. For cresol red it is 0.008.
t'_w is the temperature of the water at the time of measurement.
t_w is the temperature of the water at the time of collection.

Then the entire equation becomes

$$pH_{t_w} = pH_{t_b} + a(t_b - t_w) + B(t_w' - t_w).$$

The Glass Electrode (8)

It has been found that there is a difference of potential across a thin glass membrane separating two solutions. This potential depends on the difference of the hydrogen-ion concentrations in the solutions. The potential of the cell corresponds to the reversible hydrogen electrode

$$E = E_0^0 - \frac{RT}{F} \ln a_H^+ \qquad (1)$$

E = EMF of the cell
E_0^0 = standard potential of the glass employed
R = the gas constant
T = absolute temperature
F = free energy
a_H^+ = activity of the hydrogen ion (H^+)

There is no completely satisfactory explanation of why a glass electrode functions as a reversible hydrogen electrode, but it is probable that the hydrogen ions in solution exchange to some extent with sodium ions on the surface of the glass membrane. The result is that a potential, similar to a liquid junction potential is set up at each surface of the glass.

In its simplest form the glass electrode consists of a tube terminating in a thin walled bulb. The bulb contains a solution of constant hydrogen ion concentration, and an electrode of definite potential, e.g. silver chloride electrode in 0.1 N hydrochloric acid, or a calomel electrode in 0.1 N hydrochloric acid.

The bulb is inserted in an experimental solution and the potential measured by combining it with a suitable reference such as a calomel electrode. The cell is then

Calomel electrode / Solution of known pH/
Glass membrane / Solution of unknown pH/
Calomel electrode

Owing to the high resistance of the glass (10 to 100 million ohms) special methods must be employed for determining the E.M.F. of the cell; these generally employ the electrometer or vacuum tube circuits. Several commercial forms of apparatus are now available which employ robust glass electrodes, and some form of electrometer triode vacuum tubes to measure the potential to about 0.0005 volt, i.e. 0.01 pH unit without difficulty.

If both internal and external surfaces of the glass electrode were identical it follows from equation 1 that the potential of the electrode system would be determined simply by the pH of the solutions on the two sides of the glass membrane. However when the solutions inside and outside the membrane are identical the E.M.F. of the cell is found to be ±2 millivolts, when it should be zero. This small difference is called the assymetry potential of the glass electrode and is probably due to the difference in strain of the two surfaces of the membrane.

The potential satisfies equation 1 for a reversible hydrogen electrode very closely in the pH range 1 to 9 and with fair accuracy up to pH 12. In basic solutions of pH greater than 9 appreciable salt effects become evident and increase with the pH. In acid solutions of pH less than one, similar salt effects depended on the anions become evident. Aside from these limitations the glass electrode can be employed in almost any kind of aqueous solution, the electrode cannot be poisoned, and is not affected by oxidizing or reducing substances, or organic matter. It can be used in buffered solutions, and can be adapted for measurements in very small quantities of liquid.

Beckman pH Meter

Operation with five inch electrodes and extended leads.

The glass electrode consists of an infinitely thin glass membrane through which hydrogen ions can migrate under electrical pressure. When new there are few or no hydrogen ions in the membrane. In order that the transfer should be quantitative it is essential that the membrane should contain the same concentration of ions as is present inside the electrode, that is 0.1 Normal. Consequently it is necessary to soak a new electrode, or one that has not been in use for a month or more, in a solution of 0.1 Normal HCl for a period of 12 to 24 hours. After this treatment it should be rinsed at three times with distilled water and then with the test solution before use.

The electrode should be kept in distilled or soft fresh water between periods of use. If the use is frequent, semi-daily or oftener, it may be allowed to go dry, although this should be avoided if at all possible. Once the electrode is dry for a day or more it is usually necessary to give it a short treatment with 0.1 N HCl. to regenerate the concentration of hydrogen ion in the glass.

The Calomel half cell consists of a mixture of mercury and calomel which is contained in a glass tube in the center of the electrode, and is surrounded by a saturated solution of KCl which contacts the test solution through a loosely fitting ground glass joint.

When new, the ground glass joint is covered with a piece of rubber tubing, and the rubber stopper on the filling opening is bound in place. To prepare the cell for use, remove the rubber tubing on the ground glass joint and fit the glass collar snugly in place. Then remove the rubber stopper, and loosen the collar to allow a few drops of the KCl solution to run through the joint. Reset the collar so there is a film of solution remaining in the joint and replace the rubber stopper.

During operation, it is necessary to remove the stopper and loosen the collar every second or third test when the observations are being made continuously, in order to regenerate the saturated KCl solution under the collar. This electrode should never become dry when the glass collar is in place, KCl creeps and collar sieses. Cell may be left immersed in pure water, or the collar removed and the tip covered with rubber tubing.

The level of the KCl solution inside the cell should never fall below the level of the upper edge of the glass collar. The cell may be filled with a saturated solution of KCl through the filling opening. One or two tiny crystals of the pure salt should be added with the saturated solution at each filling, but the accumulation of these crystals should not be above the small hole in the ground tip.

The extended leads

The lead sockets in the front panel of the meter are not directly suited to the connection on the lead from the glass electrode. An adapter is provided having a washer connection on the one end to fit the glass electrode and a phone plug on the other end to fit the lead socket in the instrument.

The glass electrode must always be connected to the upper terminal.

A shielded cable extension lead is provided, one end of which is fitted with both washer and socket connections to fit the electrode terminals, and the other end is fitted with phone plugs to fit the meter.

The white wire connects the glass electrode to the upper lead socket in the meter.

General Operation

Put the switch in the upper left hand corner of the meter panel to position 1 and wait a few minutes until the galvanometer needle comes to rest on the scale. Adjust knob 1 and vernier until the needle rests at zero.

Hold the switch in position 2 and adjust knob 2 and vernier until the needle rests at zero.

Repeat the process of adjustment until the galvanometer needle assumes zero rest for either position of the switch.

The pH of the test solution may now be observed by placing the electrodes in the solution, pushing down on the button in the center of the large dial and rotating until the galvanometer needle assumes zero rest. It is advisable to check the zero rest of the needle at switch positions 1 and 2 after each observation. The pH is that indicated under the cross wire above the large dial.

The temperature of the test solution should be determined and the temperature compensator set at the observed value.

A glass electrode is not symetrical. That is the pH is always a little less than the amount indicated by the current flowing. This may be corrected by the use of the zero adjuster during the test of a solution of known pH.

To test the instrument, short circuit the lead sockets in the front panel of the instrument, set the temperature compensator at 20°C and the pH should read 7.8 or can be brought to this value with the zero adjuster. In this test it is usually only necessary to observe that the pH lies close to this value, viz. between 7.4 and 8.2 to be assured that the meter is in serviceable condition.

If the movements of the galvanometer are erratic a loose connection is indicated. Check over all outside connections and if necessary raise the instrument panel and inspect the battery connections.

COLORIMETRIC ANALYSES (5)

In general, colorimetric analysis consists in adding a reagent to a solution of the test substance in such a way as to produce a color. The basis of colorimetry may be stated as follows: When equal heights or thicknesses of two solutions give the same intensity of color, the concentrations of the solutions are said to be equal. When equal color intensity is obtained from difference heights of two solutions, the assumption is often made, in accordance with Beer's law, that the concentrations are inversely proportional to the heights. While many colors follow Beer's law sufficiently closely, recent colorimetric work makes no assumption at all. The amount of color for each concentration is obtained by standardization with each substance under the conditions found in any particular determination.

As a matter of convenience, and also to insure greater precision and speed, special forms of apparatus have been developed for use in colorimetry. Many of the more commonly used instruments are described in detail in the literature. The methods employed in matching colors may be grouped under four heads:

1. Standard series method.
2. Dilution method.
3. Duplication method.
4. Balancing method.

Standard Series method In this method the sample solution contained in a glass tube (or cell) is diluted to a definite volume, mixed, and its color compared with a series of standards similarly prepared.

In some cases it is possible, and may be more convenient, to prepare a series of permanent standards by means of solutions and mixtures of solutions of certain colored inorganic salts, such as, for example, cobalt chloride, ferric chloride and copper sulfate.[2] If such a series is employed, each solution must, of course, be standardized against a known amount of the original substance and under identical conditions as maintained in the analysis of a sample of the substance. Care must be taken that the tint or shade of color is the same in the permanent standard as in a solution of the substance to be determined.

Sometimes it is a great convenience to use a series of colored glasses as standards. For example, cobalt glass has been found to match the blue color of certain vat dyes reduced by alkaline sodium hyposulfite.[3] The use of these permanent standards proved a great help in reaction velocity studies on these dyes where it was necessary to make rapid determinations every few minutes and, also, on account of the fact that the reduced dyes are readily oxidized by air, and therefore a freshly prepared standard would be required for each determination. The plates of glass were standardized against known weights of dye reduced under standard conditions and were always placed in the colorimeter in a definite position to guard against introducing an error due to any irregularity in the glass. In using colored glasses as permanent standards, great care must be taken that the tint of color exactly matches that of the test solution. For a more detailed discussion of permanent standards consult the references on standards given in the Bibliography.

With a series of standards, the amount of substance in the sample is obtained directly, since it is equivalent to the amount contained (or represented) in the Standard which it matches in color intensity.

Dilution Method If the sample and standard solutions, when placed in glass tubes (or cells) of the same diameter and observed horizontally through the tubes, have the same intensity of color, obviously their concentrations are identical. Usually the solutions do not match in color intensity, and the darker one is then diluted until a match is obtained when the two are viewed horizontally through the tubes, i.e., through the same thickness of liquid. This process of comparison is called the dilution method. When sample and standard solutions match, their concentrations are the same, and, hence, the weights of the substance in the two solutions are directly proportional to the respective volumes.

Duplication method The sample is placed in a glass tube (or cell), diluted to a definite volume, and mixed. Water is put in a similar vessel and the same reagent (or reagents) added as used to produce the color with the sample. The volume in this "blank" should be a little smaller than that of the sample solution. Next, a relatively concentrated standard solution of the substance being determined is run into the "blank" from a burette until its color matches that of the sample solution, the final observation being made after the "duplicate" has been brought up to the same volume as the sample, by the addition of distilled water, and thoroughly mixed. The amount of standard solution required to make the "duplicate" is a measure of the amount of substance in the sample solution.

Balancing Method This method consists in placing the sample solution (or an aliquot portion) in a flat-bottom graduated tube and then running into another similar tube a standard color solution until the color intensities of the two are the same when viewed vertically through the length of the columns of liquids. When thus "balanced", the concentrations of the two solutions are inversely proportional to their heights (not volumes) in the tubes. Schreiner[4] points out that "curiously enough, the graduation into cubic centimeters has been carried over to the cylinders used in many of these instruments (balancing or plunger type colorimeters) when it is perfectly obvious that it is the height of the standard liquid which determines the strength of the unknown solution". Of course, if both the sample and standard tubes have the same diameter and the bore is uniform throughout in each tube, then the two concentrations are also inversely proportional to their volumes when the colors are matched by the balancing method. Such uniformity in color tubes is hard to obtain, and is unnecessary when the balancing method is employed, unless the highest degree of precision is required. Moreover, the use of the cubic centimeter scale in graduating the balancing or plunger type colorimetric apparatus is wrong in principle and therefore should not be employed. A rational graduation into scale divisions (say, centimeters) independent of capacity of the tube, or uniformity of bore, should be used.

Instead of placing the sample solution in the tube and changing the height of the standard column until the color intensity is the same as that in the unknown, a measured height of standard solution may be placed in one tube and the sample solution run into the other until a color match is obtained.

The balancing method is by far the speediest of the four procedures above mentioned. It is also, in general, the most accurate, provided the proper conditions are observed.

The change in the height of a solution has been accomplished in a variety of ways, e.g., (1) by dropping from a burette into one of the comparison tubes, (2) by providing one or both of the tubes with a stopcock near the bottom, (3) by connecting, by means of a side tube at the bottom, with a reservior which permits moving the solution up and down at will, and (4) by changing the height by means of an immersion prism or tube. These types of instruments are described in detail in the literature.

Requirements of the Colorimetric Method[5] In order to make possible the employment of a colorimetric method, certain conditions must be fulfilled, chief among which are the following:-

1. The color produced by the reagent must be characteristic of the test substance, or, in case certain other substances produce the same color as does the test substance, these must be known to be absent.

2. The color produced by the reagent and test substance must be the only color present in the solution. In some cases the presence of a very small amount of foreign colored substance in the sample solution may be compensated by using a standard with the same concentration of the foreign substance. For example, a titanium solution containing a small amount of ferric salts may be accurately matched against a standard titanium solution to which has been added ferric ions sufficient to equal the concentration of the latter in the test solution.

3. The sample solution must be colorless, or, if colored, this color must be removed by the reagent or by some other step in the procedure.

4. The sample solution must not contain any foreign substance which will give a color or precipitate with the reagent.

5. The color produced by the reagent must be reasonably permanent, i.e., it must not fade so rapidly that an accurate color comparison is impossible. Under certain well-defined conditions it is sometimes possible to employ a fairly unstable color and still obtain

a satisfactory quantitative measurement. Such cases will be treated in the text in their respective procedures.

6. Neither the *intensity* nor the *tint* of the color produced by the reagent and test substance must be affected by the presence of relatively high concentrations of electrolytes likely to be present. In certain cases it is necessary to adjust very carefullythe hydrogen-ion concentration before an accurate color comparison can be made.

To the above may be added certain other conditions which are desireable in a colorimetric method but which are not always required.

1. The intensity of the color should be directly proportional to the concentration of the test substance.

2. The color should be one easy to distinguish and to match; for example, blue, red,green, etc. In this connection it must be remembered that an operator may have a dull of imperfect susceptibility to one color and still be able to match other colors with great precision. It is therefore important that he test himself thoroughly for each color by matching a standard against itself in several degrees of intensity. If concordant results are not obtained with a certain color, it is useless for him to go further with this color.

3. The method should be rapid, accurate, and sensitive. Frequently one, or maybe two, of these qualities are sacrificed in order to attain the more desired third quality. In general, colorimetric methods are rapid and accurate and often are delicate enough to determine quantitatively one part of the test substance in several hundred thousand parts of water. Some are so sensitive that one part of test substance may be detected in a hundred million parts of water.

Accuracy of Colorimetric Methods No general statement can be made as to the accuracy of colorimetric methods. Some colorimetric determinations have been brought to such a high degree of prefection that they far surpass gravimetric or volumetric determinations in accuracy. On the other hand, many colorimetric methods are only rough approximations. These approximate methods, however, serve a purpose, for in such cases we frequently have no other means of determining the substance; or, as often happens, a very *rapid* method may be necessary, and a colorimetric procedure, although its results are only approximate, may meet this requirement. It is between the above two extremes of accuracy that most of the colorimetric methods lie. Attention has often been called to the extreme degree of accuracy attainable in colorimetric methods when properly carried out .... "There is little doubt that their accuracy is more frequently underestimated than overestimated. This is due to a number of causes, chief among which are the inability on the part of many persons to judge colors accurately, contamination while making the tests, the use of impure reagents, and the employment of faulty apparatus. Practice will do a great deal to enable one to make good comparisons, but it can never make up for a dulled or imperfect susceptibility to color".[6] Great attention should be given to this point in using colorimetric methods.

Speed of Colorimetric Methods As in the case of accuracy colorimetric methods vary widely from the standpoint of speed. Some are extremely rapid, required only a few minutes, while others are very slow and tedious, especially if the highest degree of accuracy is desired. Often accuracy is sacrificed for speed. "In devising colorimetric methods there have been two main objects throughout, namely, speed and ability to estimate small amounts, both of which are common to many of the methods, but not necessarily so. A colorimetric method may have speed and yet not be capable of estimating very small amounts. Speed is, through necessity perhaps, of the greatest importance to the works chemist and to the busy analyst. The ability to estimate very small amounts of material, however, is of the greatest importance to the modern investigator in the fields of pure and applied sciences, and to him speed is of a only secondary importance if indeed he values it at all. Some of the more recently devised colorimetric methods are for this very reason fully as laborious and perhaps even more tedious than the gravimetric methods, and their own virtue lies in the fact they can be used in determining amounts so small that gravimetric methods fail, and, hence, they present a means of attacking problems which hitherto had been impossible of investigation.

"The choice whether a gravimetric (or a volumetric) or a colorimetric method should be used in a given case lies therefore almost wholly within that class of colorimetric methods which have been devised for speed, and the question in this case is usually only one of comparative accuracy as balanced by the gain in time. This gain in time may, however, be of the utmost importance, not only in a works laboratory, but also in a scientific investigation where it is necessary to know the amount of a substance present at any given time in the course of an experiment".[7]

In spite of certain limitations "the colorimeter" is coming into use more and more every day because of its answer to the demand in nearly every laboratory for speed. Colorimetric methods, used because of their speed, give results in five minutes to one hour from the time the test is begun which is in all cases less than half the time similar tests could be made by other methods (except perhaps potentiometric methods). A leading brass manufactory of the country (United States) obtains an analysis of its brass from the laboratory within forty-five minutes after the delivery of the sample. Of the five constituents determined, four are determined by colorimetric methods".[8]

Limits of Application of Colorimetric Methods In general, a colorimetric method cannot be used when more than one or two percent of the substance being determined is present without resorting to aliquot parts and using a portion of the solution of the sample instead of the whole. In the latter case it is, of course, necessary to measure the aliquot part as accurately as the sample was measured, otherwise the final result will be in error.

As for the lower limit of application, it may again be pointed out that many colorimetric reactions are sensitive enough to detect one part of test substance in several million parts of water and some will detect one part in a hundred million parts of water. Hence, by using a large weight of the sample material, or a large volume in the case of solutions and then concentrating by evaporation, extremely small amounts may be determined. Of course, the size of sample that can be handled reaches a practical limit. For example, a long time is required for concentrating large volumes of liquids and great care must be taken to prevent contamination from dust particles, vessels, etc. Furthermore, various salts may crystallize out during evaporation and occlude some of the substance being sought, or a certain constituent which has no effect in the dilute sample may interfere when its concentration is increased.

In spite of the many requirements imposed upon colorimetric methods, it may be said that, in general, they are applicable to concentrations of one or two per cent down to one part in a hundred million, but these limits may be extended under proper conditions as pointed out above.

[illegible]

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Theory of Balancing Method (8,9)

Beer's law, upon which colorimetric chemical analysis is based, states that light in passing through a colored medium is absorbed in direct proportion to the concentration of the colored substance.

The expression of the relation between the incident intensity I_o and the resulting intensity I of the light passing through the medium is:

$$I = I_o e^{-pL}$$

Where p is the fraction of light absorbed in traversing unit length of the medium, L is the length of the medium, and e is the Naperian logarithmic base. But by Beer's law,

$$p = KC_1$$

Where C_1 is the concentration of the colored substance in the medium, and K is a constant.

Therefore in any column of length L_1 of a colored substance, the resultant intensity is:

$$I_1 = I_o e^{-KC_1L}$$

In a second column of length L_2 containing a concentration C_2 of the same colored substance under equal illumination, the resultant intensity is:

$$I_2 = I_o e^{-KC_2L_2}$$

If I_2 is colorimetrically matched to I_1 by altering L_1 to some new value L_2 , then

$$I_o e^{-KC_2L_2} = I_o e^{-KC_1L_1}$$

Whence:

$$\frac{C_2}{C_1} = \frac{L_1}{L_2} \qquad 1$$

Thus in colorimetric analysis, regardless of the radii of the tubes, the heights of the columns in the two matched tubes are in inverse proportion to the concentration in those tubes.

Measurement of Concentration

For the purpose of calculating the concentration of an analysed sample, the height of the residual column of solution in the comparison tube after colorimetric matching is measured in terms of the height of the standard tube. The relation between these heights, the concentration of the standard, and the concentration of the sample may be developed.

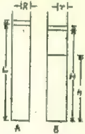

Figure 1.

Let A (in figure 1) be the standard Nessler tube containing a volume πR^2L of a standard solution of concentration C, where R is the radius of the tube and L is the standard height. Then the reagents added occupy the volume πR^2a, where a is the additional height in the tube occupied by the reagents. The concentration of the standard in A, after mixing now becomes C_A, where

$$C_A = C \times \frac{\pi R^2L}{\pi R^2L + \pi R^2a} = C \times \frac{L}{L + a} \qquad 2$$

Let B be the comparison tube containing a volume r^2H of the sample of unknown concentration C_S, where r is the radiu of the tube and H is the height to which it is filled. Then the reagents added occupy the volume πr^2b, where b is the vertical distance in the tube occupied by the reagents. The concentration of the sample in in B after mixing now becomes C_B where

$$C_B = C_S \times \frac{\pi r^2H}{\pi r^2H + \pi r^2b} = C_S \times \frac{H}{H + b} \qquad 3$$

If the tube B is now colorimetrically matched to the tube A by altering the height of the liquid (H + b) to some new value h, then from the theory of colorimetry,

$$\frac{C_B}{C_A} = \frac{C_S \times H(H + b)}{C \times L(L + a)} = \frac{L + a}{h}$$

whence,

$$C_S = C \times \frac{L}{h} \times \frac{H + b}{H} \qquad 4$$

Consideration of this equation leads to several conclusions which allow its further modification and justify some simplification of technique. It will be observed that neither the volume of reagents added to the standard nor the respective radii R and r of the standard and comparison tubes appear in the formula. However, all tubes must have a uniform radius throughout their length. For convenience of interchangability, tubes should also have a common radius in order that the standard height L will contain a common volume, and in this case tubes with 100 ml. capacity were employed.

Simplification of equation 4

(a) The volume of reagents added to 100 ml. of standard or sample is 1.0, 1.5, and 2.0 ml. in the phosphate, silicate, and nitrite tests respectively. Hence b, the height by which the reagents increase the column height H of the sample to be analysed, varies from $0.01H$ to $0.02H$. By assigning probable numerical values to formula 4, it can be seen that the adoption of a mean value of $b = 0.015H$ introduces an error of less than 0.03% in the calculated value of concentration C_S

(b) If the radii R and r of the standard and comparison tubes are approximately equal, and since H is large as compared with b, then H can be substituted by L in formula 4 without introducing a serious error in the calculated concentration C_S. Between the liberal limits of $H = (1 \pm 0.1)L$, this error does not exceed 0.2%.

Therefore, by means of the above two approximations, formula 4 can now be modified to

$$C_S = C \times \frac{1.015\ L}{h} \qquad 5$$

which is the final formula used in phosphate, silicate, and nitrite determinations. It defines the sought concentration C_S in terms of the concentration C of the standard, the standard height L, and the height h of the liquid in the comparison tube after color matching.

Balancing method with distilled water standards

It is evident from (b) that the comparison tube used need not be filled to any exact height, providing this height is within 10% of the standard height L. This tolerance is of considerable advantage when working aboard ship.

The same tolerance applies to standards prepared by dilution of a known volume of concentrated standard with distilled water in the standard Nessler tube. Precise dilution to the desired concentration (i.e., to standard height L) is unnecessary since 10% error in the volume of distilled water used does not appreciably affect the color intensity of the light transmitted through the length of the column. However L must be retained in formula 5.

When using standard solutions already made up to working concentrations, it is essential to fill the standard Nessler tube to exactly the height L.

To facilitate the procedure, ungraduated, tall comparison tubes with side arms placed about 2.5 cm. from the bottom are provided. Rubber tubing with a pinch cock fitted to the side arm permits the level of the liquid in the tube to be lowered without removing the tube from the colorimeter. A set of tall matched 100 ml. Nessler tubes made of the same glass as the comparison tubes, serve as standard tubes.

In practice, the standard solution is placed in one of the Nessler tubes, and the samples are treated in the side arm comparison tubes. The standard and one of the treated sample are placed in the colorimeter and the liquid in the comparison tube lowered by means of the side arm until the intensities of the color in the two tubes appeared to be identical. The required measurements are then made.

Method of increments (8,9)

In sea water chemistry it is frequently impossible to prepare satisfactory colorimetric standards from distilled water because of the "salt error" in the color developed.

The concentration of the sought constituent may be determined by noting the proportional increment in concentration resulting from the addition of a known amount of that constituent to the sample.

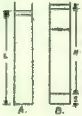

Figure 2.

Let A (in figure 2) be a Nessler tube of radius R, and filled to the standard height L with a sample of sea water containing an unknown concentration C , of the substance being investigated. Then, after mixing with the necessary reagents, which occupy an additional height a in the tube, the concentration of the constituent in A then becomes C_A , where analogous to equation 2.

$$C_A = C \times \frac{L}{L + a} \qquad 6$$

To a second B with radius r add a measured volume of a standard solution containing a concentration P of the constituent. Let this volume occupy a height S in the tube. Then add some volume of the same sea water sample as in A , increasing the liquid column in B by a height h . After mixing with the necessary reagents, which occupy a further height b, the concentration of the constituent in B now becomes C_B., where

$$C_B = \frac{C\pi r^2 H + P\pi r^2 S}{\pi r^2 (H + S + b)} = \frac{CH + PS}{H + S + b} \qquad 7$$

If the tube B is now colorimetrically matched to the tube A by altering the height H + S + B to some new value h , then from equation 1

$$\frac{C_B}{C_A} = \frac{\dfrac{CH + PS}{H + S + b}}{C \times \dfrac{L}{L + a}} = \frac{L + a}{h} \qquad 8$$

whence substituting for C from 6 and approximating

$$C_A = \frac{PSh}{L(H + S + b) - Hh} \qquad 9$$

This relation may be simplified by imposing certain conditions of technique. Thus if A and B are chosen as to identical Nessler tubes with their standard height L containing 100 ml., then the heights L , S , and b may be conveniently measured as the ml. of volume contributing these heights. Further, if in making up the tube B , the volume of sea water added increases the column of liquid to exactly the standard height L , then equation 9 becomes

$$C_A = \frac{PSh}{L(H + S + b) - hH}$$

and setting

$$H + S = L = 100$$

whence

$$H = 100 - S$$

and the equation becomes

$$C_A = \frac{PSh}{100(100 - b) - h(100 - S)} \qquad 10$$

The concentration in tube B is (from equation 8)

$$C_B = \frac{L}{h}C = 100\frac{C}{h} \qquad 11$$

The height (h) of tube (B) is read against a scale of height L divided into 100 parts from top to bottom (figure 2).

In practice one sample may be "standardized" and all other samples compared to it, or each sample may be "standardized" individually. The latter is preferable if there is sufficient sample. In any case several samples in a depth series should be standardized so that comparisons can be made among samples of comparable concentration. This avoids errors inherent in comparing columns of widely different heights.

<u>Application of equation 10</u>

A graphical representation of equation 10 proved to be of service in the selection of the concentration P and the volume S of the standard solution most suitable for the enrichment of the sea water sample being standardized. Figure 3 shows the relation of C to h as S varies while P = 1 and b = 1. For any available concentration nP, the same curves apply if the ordinate C be multiplied by the factor n. Similar curves may be constructed for tests in which b has a value other than 1, although the shape of the curves remain very similar to those in figure 3. The use of the graph may be illustrated by an example as follows:

In preparing a sea water sample standard for a phosphate determination on a series of samples of suspected concentration range of 0.001 to 0.002 mg. atoms of PO_4 per liter, a portion of the sample with the highest probable concentration in chosen for the standardization.

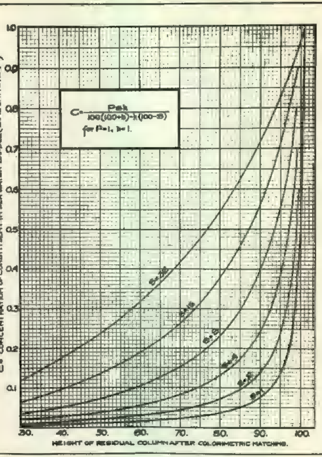
$C = \frac{PSk}{100(100+k) - h(100-S)}$
for P=1, k=1.
S=20
S=15
S=10
S=5
S=2
S=1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
30.
40.
50.
60.
70.
80.
90.
100.
C = CONCENTRATION OF CONSTITUENT IN SEA WATER SAMPLE (SAME UNITS AS P)
HEIGHT OF RESIDUAL COLUMN AFTER COLORIMETRIC MATCHING.

FIGURE 3

From the figure, after multiplying P and ordinate C by 0.01, the ordinate for $C = 0.002$ is seen to cut the curve $P = 0.01$ and $S = 4$ in such a way that the slope dc/dh has a small value permitting of accurate visual comparison, and that the height h after matching will be considerably more than 50, even if the concentration should prove to be less than that suspected. Hence 4 ml. of a known standard solution of phosphate containing 0.01 mg. atoms of PO_4 per liter is a suitable amount of standard to be used for the enrichment of the sample. After the addition of the required 96 ml. (100 -4) of sea water and one ml. of reagents, suppose the matched height h proves to be 85. From equation 10, or by the graph, the concentration in the original sample is found to be 0.00175 mg. atoms of phosphate ion per liter.

Should this sample of standard prove to be too dilute for use with certain of the samples in the series, the enrichment standard contains, by equation 11, a concentration of 100 x .0017/85 which equals 0.00206 mg. atoms of phosphate ion per liter. The remaining samples may now be matched against either of the above two standards according to equation 5.

Precautions

In employing the method of standardisation just described, it is essential that all quantities be measured as accurately as possible. An error of one scale division in reading h, causes an error of several percent in the calculated concentration. When time permits, the mean of several complete standardisations of the sample of sea water should be ascertained.

Equations 4 and 9 are derived from theoretical considerations which do not include the effects of the nature of the chemical reactions involved in the production of the color, nor the optical molecular extinction coefficient of the dissolved colored substance. The latter gives rise to anomalies in Beer's law and consequent lack of strict applicability of the fundamental equation (1) from which equation 4 and 9 are derived. Consideration of the function of the molecular extinction factor will show that its effect is best minimised by not allowing the height h to become less than 0.5L, in the course of colorimetric comparisons.

Any non-proportionality of color developed to the concentration of dissolved substances producing the color, may be largely attributed to the above two effects and leads to appreciable errors, particularly in the nitrite and phosphate tests. These errors are of course superimposed over all those of technique.

GENERAL PROCEDURE (8)

Most colorimetric analyses of sea water are for the determination of the dissolved inorganic food materials. Since these are present in very low concentrations and there are many microscopic forms of life utilizing them, there concentration is a dynamic condition and changes very rapidly after the sample has been removed from its environment.

It has been noticed that the concentration of the disolved phosphate and silicate in a sample which has been kept for 5 hours, as compared with that of a fresh sample, may vary more than 100%. It has also been observed that if the samples are kept at room temperature (15°C.), the concentration of these constituents falls rapidly to a minumum in 6 hours, after which it rises slowly to a maximum in about 36 hours.

It is of great importance to note that the samples should be kept at their temperature in situ as nearly possible and that the analysis should be commenced within 20 minutes of their collection. The temperature difference between standards and samples should be as small as practicable at the time of the analysis (less than 2°C. difference).

Standards

The preparation of the artificial standard solutions used is described under the sections devoted to that particular analysis. Since these standards are of very low concentration, particular attention is given to their preservation. One drop of toluol or chloroform per liter is found to ensure their sterility. All standards should be kept in amber coloured glass-stoppered bottles. In practice, a seperate labelled pipette is provided for each standard solution. These pipettes should be rinsed with a few ml. of the solution before they are used, and placed in a suitable rack to drain after use.

The relatively high concentrations generally encountered in analysing the waters of the Strait of Georgia for their minor constituents have made the determinations of the blank value of the reagents a matter of lesser importance than that attached to determinations of such values in other laboratories. For the type of investigation described in this paper, the blank error was found to be negligible. Excellent methods of compensating for blank errors are available in the literature; See King 1931 and Cooper 1933.

If completley artificial standards are employed, the measured volume of concentrated standard is diluted with distilled water to approximately the 100 ml. graduation mark on the Nessler tube at the time of the analysis. In making up seawater standards however, the dilution of the measured volume of concentrated artificial standard with sea water is of necessity exact.

THE DETERMINATION OF SILICATES IN SEAWATER (1,2,8)

The presence of dissolved silicate in natural waters has been recognized since 1770 (4). The first quantitative data were obtained by gravimetric methods (9). Although refinements of the gravimetric method have been made, the procedure may still be criticezed because of the large volume of water sample required, the great length of time necessary for the completion of the analysis, as will as the lack of sensitivity and accuracy in the determination of such small amounts of silica.

A colorimetric method (6) for the determination of dissolved silicate in mineral waters was modified and made practical for routine analysis by Dienert and Wandenbulcke(5). Atkins (3) was the first to apply this method to oceanographic work. This method depends upon the formation of a yellow heteropoly acid having the probable formula $H_8Si(Mo_2O_7)_6$(8) when an acidified solution of the soluble silicate is treated with ammonium molybdate. The comparison of unknown and standard may be made in a colorimeter, photometer or Nessler tubes. Standards have been made from sodium silicate, picric acid (7) or potassium chromate (1). This colorimetric method is more accurate than the gravimetric procedure and is particularly advantageous because of the small amount of sample required and the ease and rapidity of manipulation.

Standards and Reagents

Sulfuric Acid: Dilute 1 volume of concentrated H_2SO_4 with 1 volume of H_2O.

Ammonium Molybdate: 10 grams of ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ are dissolved in 90 grams of freshly distilled water. The reagent should be examined from time to time to insure its freedom from silicates.

Preferred Standard of Potassium Chromate: Purify some K_2CrO_4 by recrystallization. Dry at 105°C. Dissolve 0.652 g. and dilute to a liter. 1 ml. of this solution is equivalent to 0.002 mgm Si. When 1 ml. is diluted to 50ml. it gives a color given by 0.040×10^{-3} mgm Si per liter of sea water. (This corrects for salt error.) Prepare an appropriate series of standards by diluting the K_2CrO_4 solution with 25 ml. of 1% borax solution and then diluting to 50 ml. (40 to 70×10^{-3} mgm Si per liter of sea water is the normal range though for ocean water, practically no silicate is present in surface waters and as much as 200×10^{-3} mgm may be present in bottom waters).

Alternate Standard: 267.3 milligrams of the recrystallized (9) vacuum dried, picric acid are dissolved in distilled water and made up to a volume of exactly 1 liter. 80 ml. of this solution are diluted to a volume of 1 liter. 1 ml. is equivalent to 0.0005 mgm Si (corrected for salt error).

Procedure

to 50 ml. of sea water freshly sampled and secured directly from the sampling apparatus as it arrives aboard ship, 2 ml. of the ammonium molybdate reagent are added and four drops of 18 NH_2SO_4. After the elapse of 5 minutes, the resulting color is compared with an appropriate series of chromate standards.

Notes on the Determination

1. Both the meta and ortho silicates are analogous in (8) their behavior toward the molybdate reagent, as might be expected since in water solution ortho silicate has been shown to be converted to meta silicate.

2. A maximum probable error of 5% occurs when Nessler tubes are employed and this may be reduced somewhat by the employment of a colorimeter or photometer.

3. The borax acts as a buffer in the regulation of the pH of the solution. This is necessary to insure a constant equilibrium between $CrO_4^=$ and $Cr_2O_7^=$.

$$2\,CrO_4^= + 2H^+ \rightleftharpoons Cr_2O_7^= + H_2O$$

4. The ordinary C.P. picric acid contains varying quantities of water (7) and thus the compound should never be used without first removing the water and recrystallizing from benzene. K_2CrO_4 is even easier to purify and is more certain of giving the same color in equal amounts.

5. Picric acid standards should never be prepared by dilution with sea water as the dissolved salts have a decided "salt effect" upon the tautomeric equilibrium existing in picric acid solutions. (9)

6. Picric acid standards are stable for a period of months (8), chromate even longer.

7. Sea water acts on glass; therefore, samples that have been stored in glass containers for any length of time give high results and are valueless.

8. Nessler tubes which have been used for the phosphate determination should not be used for the determination of silicon as often color difficulties are experienced if this is done.

9. A greenish tinge is sometimes obtained with water having (8) more than 7×10^{-2} mgs Si per liter, especially when Nessler tubes are employed. This interference may be eliminated by the use of the photometer or by proper dilution of a smaller water sample.

10. Should it be deemed desirable to dilute samples high in silicon with distilled water, a test should first be made on the latter to ascertain the presence or absence of silicates.

11. With waters of low silicon values, 100 ml. samples should be utilized. A sensitivity is obtained with Nessler tubes equivalent to 2 parts of Si in 1000,000,000 parts of water.

12. Temperature has little effect upon the color intensity of (9) the yellow heteropoly acid.

13. An excess of sulfuric acid causes a diminution in the color intensity but no effect is noted with slight excesses of the molybdate reagent (8). The yellow color of the heteropoly acid reaches its maximum intensity within 5 minutes after the addition of the reagents and remains constant for nearly three hours. However, the samples should be compared with standards as soon as possible to avoid any increase in silicate concentration by the action of the sea water on the glass containers.

14. While the presence of compounds of iron and phosphorus may interfere with the determination (9), their occurrence in sea water is of such a concentration that any error from this source is negligible.

15. The silicon should be reported as milligram atoms of silicon per liter of water.

16. Silicates are utilized by phyto plankton, sponges, etc., to form the silica spicules, or frame work for the protein body. Low silicate concentration in the photo synthetic zone is usually associated with existing or immediately previous plankton blooms. Lack of silicate can be a limiting factor in plankton growth. The high silicate concentrations in deep waters are associated with the dissolution of plankton sinking from the photosynthetic zone. The concentrations in the latter zone are regenerated by mixing and upwelling.

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[redacted] (1,2,5,8)

The concentration of PO_4 in sea water varies from 0.000 to about 0.002 gram atoms phosphate-phophorous per titer at 20°C. For the determination, the method of Deniges's as modified for the purpose is recommended. The method itself is based on the principle that when a sulphuric acid solution of ammonium molybdate is added to a soluble phosphate solution a complex phosphomolybdic acid is formed. Upon treatment with a reducing agent such as stannous chloride, the complex acid is reduced to a blue colored substance believed to have the composition $H_3PO_4.(4MoO_3.MoO_2)_2.4H_2O$. The color developed is proportional to the concentrations of the phosphate.

Arsenates give similar reactions with the ammonium molybdate and stannous chloride solutions. Arsenates, if present in sea water, occur in extremely small concentrations, probably less then 0.0005 g. atoms of arsenate-arsenite per liter of sea water. The procedure here given determines the sum of the arsenates and phosphates. For sea water containing more than 0.001g. atoms of phosphate phosphorous, the arsenates may be ignored, as the experimental error of the method will be greater than the actual amount of arsenic present.

The phosphorous and arsenic contained in organic compounds dissolved in the sea water, and in inorganic compounds other than phophates and arsenates, have no influence upon the intensity of the blue color developed by the reagents.

Reagents

Reagent 1.

A sulphuric acid solution of ammonium molybdate is prepared by dissolving (a) 11.3 grams of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 100 ml. of distilled water at 60° C. and (b) 140 ml. of concentrated sulphuric acid in 400 ml. of distilled water. When both solutions are at room temperature, the first (a) is slowly added to the second (b) with stirring, and when the solution is cool, it is diluted to one liter with distilled water.

Reagent 2.

A freshly prepared solution of stannous chloride is made by adding 3.3 grams of mossy tin to 30ml. of concentrated HCl and covering the solution with a thin layer of mineral oil (Mohr seal). The solution is conveniently effected by allowing the flask to remain in a warm place for 24 hours. 250 ml. of distilled water is boiled and allowed to cool under a similar of mineral oil. When the water is cool, the stannous chloride solution is then added and the mineral oil is allowed to remain on the surface of the mixture. It is advisable to make up this solution at frequent intervals and to store it in amber colored glass-stoppered bottles.

Alternatively this reagent may be prepared by dissolving 2.15g. of anhydrous $SnCl_2$ in 20 ml. of 12N HCl and diluting to 100 ml. with cooled, previously boiled distilled water. A piece of Mossy tin (Sn) is placed in the solution to retard the oxidizing effects of the air.

Standards.

A stock solution is made containing one gram of phosphate ion per liter; dissolve 2.2009 grams of microcosmic salt $NH_4NaHPO_4.4H_2O$ with distilled water and dilute to exactly one liter.

The concentrated standard used in practice is made from this stock solution as required by diluting 1 ml. to 1 liter with distilled water and preserving with a drop of toluene.

X ml. of this concentrated standard diluted to 100 ml. with distilled water in the Nessler tube at the time of the analysis gives a working standard of concentration of 0.01X mg. of phosphate ion per liter.

When the mg. atom unit is to be adopted, the concentration of the standards are changed to intregal values of this system. The stock solution is made up to contain 10 mg. atoms of phosphate ion per liter; dissolve 2.0914 grams of the microcosmic salt in distilled water and dilute to exactly 1 liter. The preparation and dilution of the concentrated standard to provide working standards is similar in every respect to that described in the previous paragraph.

One ml. of the first described standard solution diluted to 1052 ml. provides a standard solution containing 9.01 mg. atoms of phosphate ion per liter.

Such standards are found to be suitable for use in the analysis of fresh or slightly brackish water samples, but are not satisfactory for sea water analysis, where the use of sea water standards are found to be preferable. The latter are prepared by standardizing a sample of sea water empolying the method of increments.

Procedure

To each 100 ml. sample of sea water and appropriate standard, add 1.0 ml. of reagent 1 and one drop of reagent 2. The solutions thus treated are thoroughly mixed and the blue color produced in the sample is compared with that of the similarily prepared standards after 5 minutes and before 10 minutes from the time the samples are treated.

It is found convenient to add reagent 2 from a short stemmed dropping funnel in which a small quantity of the reagent is kept under mineral oil. The use of a pipette is thus eliminated.

A blank test on the reagents should be made in distilled water, and corrections noted.

Errors

From recent experimental evidence it would appear that the absolute error in a determination is not greater than 10% from all causes, and that the proportional error is within 8%.

DISSOLVED NITRATES (8)

The reduced strychnine method (Harvey 1926; Cooper 1932) with certain modifications by Riddell (1936) is used.

Reagent I: 150 g. of iron-free granulated or foil zinc is washed with dilute HCl, then with 100 mls. of saturated $HgCl_2$ solution, and then completely rinsed with distilled water. The amalgamated zinc is transferred to a well rinsed flask 1.5 liter capacity, containing 25 ml. of H_2O distilled over baryta, 2 g. of strychnine sulphate is added and the flask placed on an electrically heated water bath at about 65°C. Between 150 and 200 mls. of concentrated HCl is added in 50 ml. portions from time to time as required for a steady generation of hydrogen. Complete solution of the strychnine and zinc requires from 12 to 24 hours, during which time the flask is covered with a beacker and no flames should be present in the room. The heating may be interrupted. The solution is finally evaporated to a small volume until an olive-green color just commences to be evident. After cooling, 1 liter of special nitrogen free H_2SO_4 is added. This operation should be preformed in the open since considerable ebullition takes place.

Nitrogen free H_2SO_4 may be satisfactorly prepared from ordinary chemically pure H_2SO_4 by heating at 300°C for 1 hour with a few crystals of $(NH_4)_2SO_4$.

Reagent II: Concentrated hydrochloric acid.

Standards

1. Absolute standards: A concentrated stock solution containing 10 mg. atoms of NO_3 nitrogen per liter (1.0111 gms. of recrystallized KNO_3) is prepared. This stock solution is diluted to give concentrated standards containing 0.002, 0.004, 0.008, 0.01, 0.02 and 0.04 mg. atoms of NO_3 nitrogen per liter.

2. Standardized sea water: If NO_3 free sea water is not available for preparing absolute nitrate standards and rather than rely on the standards prepared from distilled water, it is advisable to standardize a sample of sea water by the method of increments.

In carrying out the latter procedure the use of a solution containing 0.01 mg. atoms of nitrate nitrogen per liter is prepared by diluting 1 ml. of stock solution to one liter. This solution is sufficiently concentrated for enrichment of the sea water standard, without unduly lessening its total salt content.

Apparatus

The necessary apparatus consists of a Dubosq colorimeter and a sufficient number of cups or plane-bottomed glass vials to accommodate a complete series of analysis of samples and standards concurrently.

The colorimeter is mounted on a board to which an incandescent lamp is fitted on a slide so constructed that the distance of the lamp from the colorimeter can be varied between 10 and 30 cm. A cover is placed over the lamp so that the light shines only on the reflector of the colorimeter.

Glass vials were temporarily used during one investigation, but Dubosq cups made of one piece of glass with opaque sides and tops are preferable. Each vial or cup should be supplied with a small glass stirring rod.

The bottoms of the vials are fitted into a wooden block to which is hinged a second block with corresponding holes to receive the tops. Small orifices in the cover permits drainage of the vials after washing and inversion of the block. This protecting block provides the insulation desirable for conserving the heat of reaction during the analysis.

Procedure

1. Analysis: Seven ml. of each sea water sample and a suitable selection of standards are pipetted into the Dubosq cups which have been well washed, drained to dryness, and placed in the wooden block. To each add 7 mls. of reagent I, and 3 drops of reagent II, followed by quick and vigorous stirring. Considerable heat is evolved and the insulation and exclusion of light afforded by the wooden block is essential. The samples are compared with the appropriate standard after one hour, and before two hours.

Standard colorimetric procedure is to be followed in the comparison of the red color developed, and the glass plungers are rinsed between each analysis.

In using the Dubosq colorimeter, it is inconvenient to determine the height of the sea water alone in the cup; therefore the combined height of the same and reagents is determined at the time of the comparison.

If L represents one half of the height of the sea water, and reagents combined in the cup, h the height of liquid below the bottom of the plunger in the comparison cup after color matching, and C the concentration of the standard, then concentration Cs of the sample is

$$Cs = C \times \frac{2L}{h} \qquad \text{(cf. equation 4)}$$

The concentration thus calculated is corrected according to the curves illustrated in figure 4 by following along the horizontal line representing the apparent concentration until the curve is met and then reading the abscissa of that point on the margin where the true concentration is found.

Standardisation of sea water

Since the comparison of samples with standards of the same order of concentration is desirable, it is customary when employing standardised sea water to standardise every third or fourth sample in order of depth.

To a cup A is added 7.00 ml. of a sea water sample to be standardised. To a second cup A , 0.50 ml. to 1.00 ml. (according to suspected NO_3 concentration) 0.01 mg. atom of N per liter distilled water standard is first added, then sufficient of the same sea water sample to bring the total volume to 7.00 ml. The reagents as described for analysis are then added, and after color development the color intensity of B is matched against that of A.

Anologous to equation 10, the concentration C in the cup A is:

$$C = \frac{Pah}{2\,L^2 - h(L - S)}$$

where L is half the height of the sea water sample and reagents combined in the cup, P is the concentration of the distilled water standard added to B, S is the height in cup B occupied by this standard, and h is the height of liquid below the plunger in tube B after matching.

The volume of S is more conveniently determined as:

$$S = \frac{L \times \text{ml. of distilled water standard added}}{14}$$

The concentration in tube A thus calculated is finally corrected by means of the graph shown in figure 4.

Error

The accuracy of this analysis is entirely dependent on close adherence to the outlined procedure. If the color developed appears to have an orange tint instead of being pink or red, the analysis should be repeated, as this indicates faulty procedure.

It is realised that the height occupied by reagent II in neglected in the formulae. Its volume acts as a correction for the amount of liquid lost by evaporation when the sample is at a high temperature when treated with reagents.

Check analysis consistent within 6% can be obtained under working conditions at sea, and it is assumed that this is the limit of normal error in this test.

THE DETERMINATION OF NITRITES IN SEA WATER (5)

The concentration of nitrite-nitrogen in sea water varies from 0.000 to 2.00 microgram atoms per liter of sea water at 20°C. In the open ocean nitrites are seldom found in depths below 100 meters, and even at these depths the water maybe completely devoid of nitrites. When occuring in waters near the surface, the concentration is generally less than 0.10 u.g. atom of nitrite-nitrogen per liter. The higher values are obtained at times in the waters on the continental shelf and in sounds, straits, fjords and estuaries.

The method recommended for the determination of nitrites is shown by the chemical equation:

$$HSO_3.C_6H_4.NHO_2 + C_{10}H_7.NH_2 \rightarrow HSO_3.C_6H_4.N{:}N.NH.C_{10}H_7 + 2H_2O$$

and was originally developed by Peter Greise and later modified by Ilosvay (1889). This method depends upon the diazotazation of the amines in acid solution by the nitrite in the sea water. The product of this reaction is a rose-colored dye whose color intensity is proportional to the quantity of nitrite present.

Reagent 1 0.40 grams of Alpha Napthylamine is boiled with 80 ml. distilled water. The colorless solution is decanted while hot from the dark precipitate and treated with 30 ml. glacial acetic acid. The solution is diluted with 285 ml. distilled water, and stored in a glass stoppered amber bottle.

Alternatively one ml. dimethyl-alpha-napthylamine is dissolved in a solution of 50 ml. glacial acetic acid and 170 ml. of methyl alcohol. The reagent should be made fresh monthly, and stored in a glass stoppered dark bottle.

Reagent 2 2 grams sulphanilic acid is dissolved by heating in a solution of 80 ml. glacial acetic acid and 80 ml. distilled water. More water is gradually introduced to the warm solution with constant stirring until 140 ml. have been added and the sulphanilic acid is dissolved. The solution should be kept in glass stoppered amber bottles and made fresh monthly.

Note Occassionally it is difficult to obtain distilled water free of nitrites. Suitable water may be prepared by redistilling after making alkaline with sodium hydroxide or barium hydroxide.

Standard Nitrite Solutions

Standard solution I (stock solution) 0.690 g. pure $NaNO_2$, previously dried for 4 hours at 110°C and cooled in a dessicator, is dissolved in nitrite free distilled water, and made up to one liter. 0.2 ml. chloroform or carbon disulphide added as preservative will maintain stability for several months.

1 ml. contains 10 microgram-atoms of nitrite-nitrogen.

Standard solution II Dilute 10 ml. of standard I to 1000 ml. with nitrite free distilled water.

1 ml. contains 0.10 microgram-atoms of nitrite-nitrogen.

Standard solution III Dilute 0.1 to 100 ml. of standard II to 100 ml. in Nessler tubes as required for analyses.

Procedure

To each 100 ml. sample of sea water add one ml. of reagent I and one ml. of reagent II. Mix thoroughly and allow to stand and compare with a similarly treated standard after at least one hour.

Notes

1. The samples for the nitrite determinations are to be treated with reagents as soon as possible after collection. The color is stable for four or five days, hence comparisons may be made at leisure.

2. The maximum color intensity is attained in about 30 minutes in sea water, but requires one to two hours in distilled water. The intensity of color developed is the same in either case for a given nitrite concentration. The rate of color development increases with temperature, hence temperature variation between samples should not exceed 2°C.

3. The method of increments is particularly suited to this nitrite analyses, because of the salt effect on the reaction rate, and the wide variance of concentration normally encountered in a series of samples from successive depths in the sea.

4. The bright red color developed in this analysis permits easy and accurate comparison. It appears that the test is entirely selective, and unaffected by normal variations in temperature, or of other constituents in the water. The color developed is directly proportional to the concentration of nitrite-nitrogen. The total error is usually less than 5%.

5. The presence of nitrites imply reducing agents such as decaying organic matter, and are usually found below the plankton layer, at great depths, in stagnant water, or in the presence of domestic or industrial pollution. They are usually associated with low oxygen concentrations.

MEASUREMENT OF TEMPERATURE (1,2,3)

Four methods are used for measuring sea temperatures.

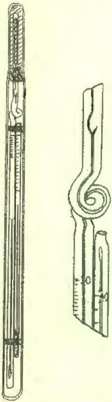
1. Ordinary thermometers are employed for observing surface temperatures in a bucket (1) or are installed in the cooling water intake to the ship's engines. These were formerly utilised for depth temperatures in insulated water sampling bottles, and corrections made for adiabatic cooling of the water.

2. A great variety of electrically, and clockwork thermographic instruments are available for use in fixed positions and attached to ship's hulls.

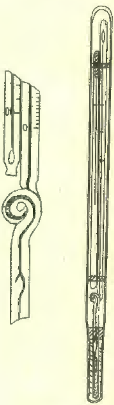
3. Protected reversing thermometers are used extensively to obtain the temperature at any desired depth (2).

4. The bathythermograph is a mechanical instrument which provides a graph of the temperature-depth relation when lowered into the sea (3).

MEASUREMENT OF TEMPERATURE
WITH THE
PROTECTED DEEP SEA REVERSING THER[redacted] (1,2,3)



Reversed



Upright

The protected reversing thermometers are used very extensively to obtain the temperatures at any desired depth. In reality each one consists of two thermometers, the reversing thermometer proper and the auxiliary thermometer. These are sealed in a heavy glass tube in order to prevent the pressures at the greater depths from having an effect upon the mercury bulbs proper. The larger bulb of the reversing thermometer is immersed in a mercury jacket contained in the heavy glass tube. This arrangement permits rapid conduction. The capillary tube of this thermometer is contracted just above the large bulb so that when the instrument is inverted the column of mercury breaks at the contraction. Part of the mercury falls into the small bulb and overflows, filling part of the graduated stem. The actual volume of mercury flowing into the small bulb is dependent upon the temperature of the mercury at the time of reversal of the instrument. The scale on the thermometer has the lowest values at the small bulb, but the stem in graduated with respect to the mercury contained originally in the large bulb. A correct readin of the thermometer is possible only when it is read at exactly the same temperature as that at the time of reversal and when the graduations are exact. If the temperature at the time of reading is greater than at the time of reversal, the mercury in the small bulb will have expanded. To obtain the actual temperature, a correction for this must be made and the purpose of the auxiliary thermometer is to give a means for making this correction. A change in the volume of the mercury corresponds to a change in temperature as recorded on the scale of this thermometer, while in the reversing thermometer, a change affects only that portion of the mercury contained in the smaller bulb after the thermometer has been reversed. The two thermometers will have the same reading at the time when the mercury column of the reversing thermometer is broken by reversal, and any differences between their readings at any other temperature will be proportional to the difference between this temperature and that at the time of reversal. This ratio is a function of the volume of mercury in the smaller bulb and the capillary of the reversing thermometer. If the thermometers are read simultaneously, a means is provided whereby the temperature at the time of reversal, or in other words the actual temperature of the water, may be computed.

Correction of Reversing Thermometers

Two corrections must be applied to the readings of reversing thermometers, namely, the index correction and the temperature-difference correction (the difference between the reading of the reversing thermometer and the auxiliary thermometer).

The Index Correction, I, is determined by the actual calibration of the thermometer at different temperatures and is dependant solely on the thermometer reading. The correction arises from the slight irregularities in the capillary tube of the thermometer. Many of the reversing thermometers in use have been calibrated by the United States Bureau of Standards, the Physikalisch-Technische Reichsanstalt (P T R), or the National Physical Laboratory (Great Britain). Upon calibration, these laboratories furnish certificates giving the corrections necessary for several readings of the thermometer. This correction, or index correction, must be added or subtracted. Upon testing reversing thermometers, these laboratories may subject them to a pressures test and the certificate of calibration may bear a phrase: "The action of this instrument was found to be satisfactory after being submitted to a pressure of 3 tons per square inch." Such a statement indicates that the thermometer may be used down to depths approximately of 4500 meters without fear of crushing the thermometer by hydrostatic pressure.

The Temperature-Difference Correction is a correction made for the expansion of mercury in the main thermometer and is a function of the amount of mercury in the smaller bulb and the capillary tube; the difference in the temperatures of the main thermometer and the auxiliary thermometer and the nature of the glass comprising the thermometer. If a thermometer is reversed in a layer of cold water and then brought to the surface through a layer of warm water, the mercury in the bulb and capillary of the main thermometer will expand and thus the reading of the main thermometer must be corrected for this expansion. In order to do this, the volume of the thermometer bulb up to the reading 0° on the capillary must be known and such volume, designated as the degree volume, is given on each thermometer. The total temperature correction, ΔT, may be calculated from the following formula

$$\Delta T = E + I$$

where $\underline{\Delta T}$ is the total correction, $\underline{E}$ the temperature-difference correction, and $\underline{I}$ the index correction.

$$E = \left[\frac{(T' + V_0)(T' - t)}{K}\right] \left[1 + \frac{(T' + V_0) + (T' - t)}{K}\right]$$

[illegible]

T' = reading of the main thermometer after reversal.
t = " " " auxiliary thermometer after reversal.
V_0 = the degree volume of the thermometer, or the volume of mercury in the thermometer at 0°C.
K = a constant expressing the relative thermal coefficient of mercury and the glass of which the thermometer is made.

The constant $\underline{K}$ is a function of the quality of the glass comprising the thermometer. Most of the reversing thermometers in use are from Jena glass 59^{III} or Jena 16^{III}. For Jena 59^{III}, K = 6100, and for Jena 16^{III}, K = 6300.

Substitution of K = 6100 in the above equation reduces it to

$$E = \left[0.000164\,(T' - t)(T + V_0)\right]\left[1 + 0.000164\,(T' + V_0) + 0.000164(T' - t)\right]$$

The temperature-difference correction, E, may be ascertained directly from the following tables by knowing the values for T', t, and V_o. The true temperature T^* may be found from the equation:

$$T^* = T' + \Delta T = T' + E + I$$

Illustration: The main thermometer reads 11.00°C, the auxiliary thermometer, 21.0°C, and the degree volume of the main thermometer is 89°C.

$$(T' - t) = -10 \qquad (T' + V) = 100$$

Reference to the table shows that E is -0.167°C and for most practical purposes becomes -0.17°C. The index correction, found by the calibration of this thermometer is +0.02°C. The total correction is:

$$\Delta t = -.17° + .02° = -.15°$$

and the true temperature

$$T^* = 11.00 - .15 = 10.85°$$

THE FUNCTION AND CARE OF REVERSING THERMOMETERS

By observing the breaking point of the mercury column in the main thermometer, namely, at the top in the coiled end of the capillary where it joins the small dead arm, it is possible to ascertain whether or not the thermometer is in proper condition.

When the thermometer is held in a vertical position with the large bulb at the bottom, there should be no air in any part of the capillary. Upon reversing the thermometer, so that the large bulb is at the top, the mercury should break at the point shown by the lower arrow in b. Observation is facilitated by the use of a magnifying glass. Upon repeating this operation very slowly, the mercury must first run out of the side arm as shown in a. During this process, care should be taken not to touch the bulb with the hand, for a temperature change makes an exact observation of the breaking point impossible. The separated column of mercury, which breaks at the side arm runs downward into the smaller bulb and graduated capillary of the main thermometer and thus corresponds to the temperature prevailing at the time of reversal. If, after breaking of the mercury thread, the thermometer is reversed to its original position, the mercury must run out of the small bulb and capillary and join the mercury in the main bulb at the dead arm. Under such conditions it may be assumed that the thermometer is functioning properly.

Improper Functioning of the Reversing Thermometer

By improper handling, such as in transportation, sudden blows or remaining in a horizontal position for a protracted period of time, the mercury may no longer form a connected thread and behave as described above. The difficulties then observed may fall into one of the three categories as follows:

a. Mercury Remains in the Upper Portion of the Smaller Bulb

If after reversing the position of the thermometer so that the large bulb is below, some of the mercury may remain in the smaller bulb. This condition is illustrated in c. In many cases, it is sufficient to reverse the thermometer again and when the mercury flowing from the large bulb is united with that which remained in the smaller bulb, the thermometer again turned to its original position, proper functioning of the mercury is observed. If this does not occur and part of the mercury still stays in the smaller bulb, a small particle of air, generally observable with a magnifying glass, is the cause of the difficulty. To remedy this situation, hold the thermometer by the large bulb in a horizontal position in the right hand and then gently tap the other end of the thermometer in the palm of the left hand until several globules of mercury separate in the small bulb as shown in d. The thermometer is then carefully inverted so that the mercury runs into the smaller bulb. As soon as it touches the small globules that have been separated, turn the thermometer again to its original position. The separated globules are thus drawn into the main bulb. Several more globules are again separated and the process repeated until all the mercury is reunited.

Under no circumstances hold the thermometer in a vertical position with large bulb downward and jar by tapping. If this is done, the air bubble may eventually be forced into the dead arm of the lower capillary and the thermometer will be ruined.

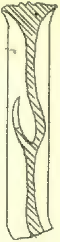
b. Mercury Remains in Smaller Bulb, Breaking at Capillary

This undesirable situation is shown in e and to remedy, hold the thermometer in a horizontal position and warm the smaller bulb over small bunsen flame, as illustrated in f, constantly rotating the thermometer. The mercury in the auxiliary thermometer rises at the same time and care must be exercised in order that no breaking of the mercury thread occurs. During the heating, the thermometer should occasionally be brought to a vertical position to see if heating has been sufficient so that the mercury runs down the capillary to the large bulb. If this occurs, the small air bubble is pushed downward into the main bulb. Examination may show that the mercury thread breaks at the proper place and that the thermometer functions normally. However, before it is used, the zero point should be checked by immersing the instrument in ice.

If the air bubble is in the looped capillary or the mercury thread does not break at the proper place, the procedure recommended below should be followed.

c. The Mercury Thread Does Not Break at Proper Place

Such a situation is illustrated in g, and to correct this defect, the thermometer is placed in a vertical position, large bulb downward, and when a continuous mercury thread has formed, cool the bulb to a very low temperature, immersing, if necessary, in a salt-ice mixture. Holding the thermometer at the looped capillary, quickly reverse it with a jerk. The thread will break at the air bubble and may also break at the usual place. After the smaller bulb is filled with the mercury, turn the thermometer to a horizontal position and warm the larger bulb slowly and carefully to about 60°C. The air bubble is driven forward. Return thermometer to original position and cool. This process of alternate cooling and heating is continued until the air bubble is above the mercury. When the thermometer begins to function normally again, it is best to check the zero reading by inserting in melting ice.



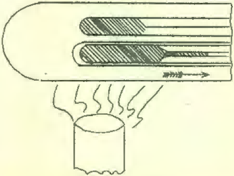
a.

b.

c.

e.

d.



f.

g.

Tables for the Temperature
Difference Correction on Protected Reversing Thermometers

	(T - t)											
(T' + V$_o$)	1	2	3	4	5	6	7	8	9	10	11	12
	Temperature Difference Correction (K)											
61	.010	.020	.030	.040	.050	.060	.070	.080	.090	.101	.111	.121
62	.010	.020	.030	.040	.050	.061	.071	.081	.091	.102	.112	.123
63	.010	.020	.030	.041	.051	.061	.072	.082	.092	.104	.114	.124
64	.010	.020	.031	.041	.052	.062	.073	.084	.094	.105	.116	.126
65	.010	.021	.032	.043	.053	.064	.075	.085	.096	.107	.118	.129
66	.010	.021	.032	.043	.054	.065	.076	.087	.097	.109	.120	.131
67	.011	.022	.033	.044	.055	.066	.077	.088	.100	.111	.122	.133
68	.011	.022	.033	.044	.056	.067	.079	.090	.101	.113	.124	.135
69	.011	.022	.034	.045	.057	.068	.080	.091	.102	.114	.125	.137
70	.011	.022	.034	.046	.057	.069	.081	.093	.104	.116	.127	.139
71	.011	.023	.035	.047	.058	.070	.082	.094	.106	.117	.129	.141
72	.011	.023	.035	.047	.059	.071	.083	.095	.107	.119	.131	.143
73	.012	.024	.036	.048	.060	.072	.084	.096	.109	.121	.133	.145
74	.012	.024	.036	.048	.061	.073	.086	.098	.111	.123	.135	.147
75	.012	.024	.037	.049	.062	.074	.087	.099	.112	.124	.136	.149
76	.012	.025	.037	.050	.063	.075	.088	.101	.113	.126	.138	.151
77	.012	.025	.038	.051	.064	.076	.089	.102	.115	.128	.140	.153
78	.012	.025	.038	.051	.064	.077	.090	.103	.116	.129	.142	.155
79	.013	.026	.039	.052	.065	.078	.091	.104	.118	.131	.144	.157
80	.013	.026	.039	.052	.066	.079	.093	.106	.120	.133	.146	.159
81	.013	.026	.040	.053	.067	.080	.094	.107	.121	.134	.148	.161
82	.013	.026	.040	.054	.068	.081	.095	.109	.123	.136	.150	.163
83	.013	.027	.041	.055	.069	.082	.096	.110	.124	.138	.152	.165
84	.013	.127	.141	.055	.070	.083	.097	.111	.126	.140	.154	.168
85	.014	.027	.042	.056	.071	.085	.099	.112	.128	.142	.156	.170
86	.014	.028	.043	.057	.072	.086	.100	.114	.129	.143	.157	.172
87	.014	.128	.043	.058	.073	.087	.101	.115	.131	.145	.159	.174
88	.014	.028	.044	.059	.074	.088	.102	.117	.132	.146	.161	.176
89	.014	.029	.044	.059	.074	.089	.103	.118	.133	.148	.163	.178
90	.015	.029	.045	.060	.075	.090	.105	.120	.134	.150	.165	.180

|T - t|

$(T' + T_0)$	1	2	3	4	5	6	7	8	9	10	11	12
Temperature Difference Correction (E)												
91	.015	.030	.046	.061	.076	.091	.106	.121	.136	.151	.167	.182
92	.015	.030	.046	.061	.076	.092	.108	.123	.138	.153	.169	.184
93	.015	.030	.047	.062	.077	.094	.109	.124	.139	.156	.171	.186
94	.015	.031	.047	.063	.078	.094	.110	.125	.141	.157	.173	.188
95	.016	.031	.048	.063	.079	.095	.111	.127	.142	.159	.174	.190
96	.016	.031	.049	.064	.080	.096	.112	.129	.145	.160	.176	.192
97	.016	.033	.049	.065	.081	.097	.113	.130	.146	.162	.178	.194
98	.016	.033	.049	.065	.081	.098	.115	.131	.148	.164	.180	.196
99	.016	.033	.050	.066	.082	.099	.116	.132	.149	.165	.181	.198
100	.016	.034	.050	.067	.083	.100	.117	.133	.151	.167	.183	.200
101	.017	.034	.051	.068	.084	.101	.118	.135	.152	.169	.185	.203
102	.017	.034	.051	.068	.085	.102	.119	.136	.154	.170	.187	.205
103	.017	.036	.052	.069	.085	.103	.120	.137	.155	.172	.189	.207
104	.017	.036	.052	.069	.086	.104	.121	.139	.157	.174	.191	.209
105	.017	.036	.053	.070	.087	.105	.123	.141	.158	.175	.192	.211
106	.017	.036	.053	.071	.089	.106	.124	.142	.159	.177	.195	.213
107	.018	.036	.054	.071	.090	.107	.125	.143	.161	.178	.197	.215
108	.018	.036	.054	.072	.091	.108	.126	.145	.162	.180	.199	.217
109	.018	.037	.054	.073	.091	.109	.127	.146	.164	.182	.201	.219
110	.018	.037	.055	.073	.092	.110	.128	.147	.165	.183	.202	.220
111	.018	.037	.056	.074	.093	.111	.130	.149	.167	.185	.204	.222
112	.018	.038	.056	.074	.094	.112	.132	.130	.168	.188	.206	.224
113	.019	.038	.057	.075	.095	.113	.133	.151	.170	.189	.207	.226
114	.019	.038	.057	.076	.095	.114	.134	.153	.071	.191	.209	.228
115	.019	.039	.058	.076	.094	.115	.135	.154	.173	.193	.211	.230
116	.019	.039	.058	.077	.096	.116	.136	.155	.174	.194	.213	.232
117	.019	.039	.059	.079	.097	.117	.137	.157	.176	.196	.215	.235
118	.019	.040	.059	.079	.099	.118	.138	.158	.177	.198	.217	.237
119	.020	.040	.060	.080	.100	.119	.140	.159	.179	.199	.218	.239
120	.020	.040	.061	.081	.100	.120	.141	.160	.180	.201	.220	.241

	(T - t)											
$(T' + V_o)$	1	2	3	4	5	6	7	8	9	10	11	12
	Temperature Difference Correction (E)											
121	.020	.041	.061	.081	.101	.122	.142	.163	.183	.202	.223	.243
122	.020	.041	.061	.082	.102	.123	.143	.164	.184	.205	.225	.245
123	.020	.041	.062	.083	.103	.124	.144	.165	.186	.207	.227	.247
124	.020	.042	.062	.083	.104	.125	.145	.167	.187	.208	.228	.249
125	.021	.042	.063	.084	.105	.126	.147	.168	.189	.210	.230	.251
126	.021	.042	.063	.085	.105	.127	.148	.169	.190	.212	.232	.254
127	.021	.043	.063	.085	.106	.128	.149	.171	.191	.213	.234	.256
128	.021	.043	.064	.086	.107	.129	.150	.172	.193	.215	.236	.258
129	.021	.043	.064	.087	.108	.130	.151	.173	.194	.217	.238	.260
130	.021	.044	.065	.087	.109	.131	.152	.175	.196	.218	.240	.262
131	.021	.044	.066	.088	.109	.132	.154	.176	.198	.220	.242	.264
132	.022	.044	.067	.089	.111	.133	.156	.177	.200	.221	.244	.266
133	.022	.045	.067	.089	.112	.134	.157	.178	.201	.223	.246	.268
134	.022	.045	.068	.090	.113	.135	.158	.180	.203	.225	.248	.270
135	.022	.045	.068	.091	.114	.136	.159	.181	.204	.226	.249	.272
136	.022	.046	.069	.091	.115	.137	.160	.182	.206	.228	.251	.274
137	.022	.046	.069	.092	.115	.138	.161	.184	.207	.230	.252	.276
138	.022	.046	.070	.093	.116	.139	.162	.185	.209	.231	.255	.278
139	.023	.047	.070	.093	.117	.140	.164	.186	.210	.233	.257	.280
140	.023	.047	.071	.094	.118	.141	.165	.188	.212	.235	.259	.283
141	.023	.047	.071	.095	.120	.143	.167	.190	.214	.237	.261	.285
142	.023	.049	.072	.096	.120	.144	.168	.192	.216	.239	.263	.287
143	.023	.049	.072	.097	.121	.146	.169	.194	.218	.241	.265	.289
144	.024	.049	.073	.097	.122	.147	.170	.195	.220	.243	.267	.292
145	.024	.050	.073	.098	.123	.148	.171	.196	.221	.245	.269	.294
146	.024	.050	.074	.099	.124	.149	.173	.197	.222	.247	.271	.296
147	.024	.050	.074	.099	.125	.150	.174	.199	.224	.249	.273	.298
148	.024	.051	.075	.100	.125	.151	.175	.200	.225	.251	.275	.300
149	.024	.051	.075	.101	.126	.152	.176	.201	.227	.252	.278	.302
150	.025	.051	.076	.101	.127	.153	.178	.202	.228	.254	.280	.304

(T − t)

Temperature Difference Correction (B)

(T' + T_o)	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
61	.131	.141	.151	.161	.171	.181	.191	.202	.212	.222	.232	.242	.252	.262	.272	.282	.292	.303
62	.133	.143	.153	.163	.173	.184	.194	.204	.214	.224	.234	.246	.256	.266	.276	.286	.296	.308
63	.135	.145	.155	.166	.176	.186	.198	.208	.218	.229	.239	.249	.260	.270	.280	.291	.302	.312
64	.137	.147	.157	.169	.179	.189	.201	.211	.222	.233	.243	.253	.264	.275	.285	.296	.307	.317
65	.140	.150	.161	.172	.183	.193	.204	.215	.226	.237	.247	.258	.269	.280	.290	.301	.312	.323
66	.142	.153	.164	.175	.186	.196	.208	.219	.230	.241	.251	.262	.273	.284	.295	.306	.317	.328
67	.144	.155	.166	.177	.188	.199	.211	.222	.233	.244	.255	.266	.277	.288	.300	.311	.322	.333
68	.146	.158	.169	.180	.191	.202	.213	.225	.237	.248	.259	.270	.282	.293	.304	.315	.327	.338
69	.148	.160	.171	.183	.194	.205	.217	.228	.240	.251	.263	.274	.286	.297	.308	.320	.331	.343
70	.151	.162	.174	.186	.197	.209	.220	.232	.244	.255	.267	.278	.290	.302	.313	.125	.336	.348
71	.153	.164	.176	.188	.200	.212	.223	.235	.247	.259	.270	.282	.294	.306	.318	.329	.341	.353
72	.155	.167	.179	.191	.203	.215	.227	.238	.250	.263	.274	.286	.298	.310	.322	.334	.346	.358
73	.157	.169	.181	.193	.205	.218	.230	.242	.254	.266	.278	.290	.302	.314	.327	.339	.351	.363
74	.159	.172	.184	.196	.208	.221	.233	.245	.257	.270	.282	.294	.306	.318	.332	.344	.356	.368
75	.161	.174	.186	.199	.211	.224	.236	.249	.261	.273	.286	.298	.311	.323	.336	.348	.361	.373
76	.164	.177	.189	.202	.214	.227	.240	.253	.265	.277	.290	.303	.316	.328	.341	.353	.366	.379
77	.166	.179	.192	.205	.217	.230	.243	.256	.269	.282	.294	.307	.320	.333	.346	.358	.371	.384
78	.168	.181	.194	.207	.220	.233	.246	.259	.272	.285	.298	.310	.324	.337	.350	.362	.375	.388
79	.170	.183	.196	.209	.223	.236	.249	.262	.275	.288	.301	.314	.328	.341	.354	.367	.380	.393
80	.173	.186	.199	.212	.226	.239	.253	.266	.279	.292	.306	.319	.333	.346	.359	.372	.385	.399
81	.175	.188	.202	.215	.229	.242	.256	.269	.283	.296	.310	.323	.337	.351	.364	.377	.391	.404
82	.177	.191	.205	.218	.232	.245	.259	.273	.287	.300	.314	.327	.341	.355	.369	.382	.396	.409
83	.179	.193	.207	.221	.235	.248	.262	.276	.290	.304	.318	.331	.345	.359	.373	.387	.401	.414
84	.182	.196	.209	.224	.237	.251	.265	.279	.294	.308	.322	.336	.349	.363	.377	.391	.405	.419
85	.184	.198	.212	.227	.240	.254	.268	.282	.298	.311	.325	.340	.353	.367	.322	.396	.410	.425
86	.186	.200	.215	.229	.243	.258	.272	.286	.301	.315	.329	.344	.358	.372	.387	.401	.415	.430
87	.189	.203	.217	.232	.246	.261	.275	.289	.303	.319	.333	.348	.362	.376	.391	.405	.420	.435
88	.191	.205	.220	.235	.249	.264	.278	.292	.307	.323	.337	.352	.366	.380	.395	.410	.425	.440
89	.193	.207	.222	.238	.252	.267	.281	.296	.312	.327	.341	.356	.370	.385	.400	.415	.430	.445
90	.195	.210	.225	.240	.255	.270	.285	.300	.315	.330	.345	.360	.375	.390	.405	.420	.435	.450

(T - t)

Temperature Difference Correction (K)

(T' + T_o)	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
91	.197	.212	.227	.242	.257	.273	.288	.303	.318	.333	.348	.363	.379	.394	.409	.424	.439	.454
92	.197	.214	.230	.245	.260	.275	.291	.306	.321	.337	.352	.367	.383	.398	.413	.429	.444	.459
93	.201	.217	.232	.247	.263	.279	.294	.310	.325	.340	.356	.371	.387	.402	.418	.433	.449	.464
94	.203	.219	.235	.250	.266	.282	.297	.313	.329	.344	.360	.376	.391	.407	.422	.438	.454	.469
95	.206	.221	.237	.253	.269	.285	.301	.316	.332	.348	.364	.380	.395	.411	.427	.443	.459	.474
96	.208	.224	.240	.256	.272	.288	.304	.320	.336	.352	.368	.384	.400	.416	.432	.448	.464	.480
97	.210	.226	.242	.258	.275	.291	.307	.323	.339	.355	.372	.388	.404	.420	.436	.452	.469	.485
98	.212	.229	.245	.261	.277	.294	.310	.326	.343	.359	.375	.392	.408	.424	.441	.457	.473	.490
99	.214	.231	.247	.264	.280	.297	.314	.330	.346	.363	.379	.396	.412	.429	.445	.462	.478	.495
100	.217	.233	.250	.267	.283	.300	.317	.333	.350	.367	.383	.400	.417	.433	.450	.467	.483	.500
101	.219	.235	.253	.271	.287	.303	.321	.337	.354	.372	.387	.405	.422	.439	.455	.473	.489	.506
102	.222	.238	.256	.273	.290	.306	.324	.341	.358	.375	.391	.409	.426	.444	.460	.478	.495	.512
103	.224	.241	.258	.276	.293	.309	.327	.344	.361	.379	.395	.413	.431	.449	.465	.483	.500	.517
104	.227	.243	.261	.278	.296	.312	.330	.348	.365	.382	.399	.417	.435	.453	.470	.489	.505	.522
105	.229	.245	.263	.281	.298	.316	.333	.351	.369	.386	.404	.421	.439	.457	.475	.493	.510	.528
106	.231	.248	.265	.283	.301	.319	.337	.355	.372	.390	.407	.425	.444	.461	.479	.497	.515	.533
107	.233	.251	.268	.287	.304	.322	.340	.358	.376	.394	.411	.429	.448	.466	.484	.502	.520	.538
108	.235	.253	.271	.289	.307	.325	.343	.361	.379	.397	.415	.433	.452	.471	.489	.507	.525	.543
109	.237	.255	.274	.292	.310	.328	.346	.364	.382	.401	.419	.437	.456	.475	.493	.511	.530	.548
110	.239	.257	.276	.294	.313	.331	.350	.368	.386	.405	.423	.441	.460	.479	.497	.516	.535	.553
111	.241	.260	.279	.297	.316	.334	.353	.372	.391	.409	.428	.447	.465	.484	.503	.521	.540	.559
112	.244	.262	.281	.300	.319	.337	.356	.375	.394	.413	.432	.451	.469	.488	.507	.526	.545	.564
113	.246	.265	.283	.303	.322	.341	.359	.379	.398	.417	.436	.455	.473	.492	.511	.532	.550	.569
114	.248	.268	.286	.306	.325	.344	.363	.383	.402	.421	.440	.459	.478	.497	.516	.536	.555	.574
115	.250	.270	.289	.309	.328	.347	.366	.386	.405	.424	.444	.463	.482	.501	.521	.541	.560	.579
116	.253	.272	.292	.311	.331	.350	.370	.389	.409	.428	.448	.467	.487	.506	.525	.545	.564	.584
117	.255	.275	.294	.314	.334	.353	.373	.392	.412	.432	.451	.471	.491	.511	.530	.550	.569	.589
118	.257	.277	.297	.317	.337	.356	.376	.396	.416	.436	.455	.475	.495	.515	.535	.554	.574	.594
119	.259	.279	.299	.319	.339	.359	.379	.399	.420	.440	.459	.479	.499	.519	.540	.559	.579	.599
120	.262	.282	.302	.322	.342	.362	.383	.403	.423	.443	.463	.483	.505	.524	.544	.564	.584	.604

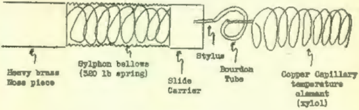
(T - t)

Temperature Difference Correction (K)

$(T' + T_o)$	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
121	.263	.284	.304	.325	.345	.365	.386	.406	.426	.447	.467	.487	.508	.528	.549	.569	.589	.610
122	.266	.287	.307	.328	.348	.369	.389	.410	.430	.451	.471	.492	.512	.533	.553	.574	.594	.615
123	.269	.269	.310	.331	.351	.372	.393	.413	.434	.455	.475	.496	.517	.537	.558	.579	.599	.620
124	.271	.292	.312	.333	.354	.375	.396	.417	.437	.458	.479	.500	.521	.542	.563	.584	.604	.625
125	.273	.294	.315	.336	.357	.378	.399	.420	.441	.462	.483	.504	.525	.546	.567	.588	.609	.630
126	.275	.296	.318	.339	.360	.381	.402	.424	.445	.466	.487	.508	.530	.551	.572	.593	.614	.635
127	.277	.299	.320	.341	.363	.384	.405	.427	.448	.469	.491	.512	.534	.555	.577	.598	.619	.641
128	.280	.301	.322	.344	.366	.387	.408	.430	.452	.473	.494	.516	.538	.559	.581	.603	.624	.646
129	.282	.303	.325	.347	.368	.390	.412	.433	.455	.477	.498	.520	.542	.564	.586	.608	.629	.651
130	.284	.305	.327	.349	.371	.393	.415	.437	.459	.481	.502	.524	.546	.568	.590	.613	.634	.656
131	.286	.308	.330	.352	.374	.396	.418	.440	.462	.484	.506	.528	.551	.573	.595	.617	.639	.661
132	.289	.311	.333	.355	.377	.399	.421	.443	.465	.488	.510	.532	.555	.578	.600	.622	.644	.667
133	.291	.313	.335	.358	.380	.402	.424	.447	.469	.492	.514	.537	.560	.582	.604	.627	.649	.672
134	.293	.315	.338	.360	.383	.405	.428	.451	.473	.495	.518	.541	.564	.586	.609	.631	.654	.677
135	.295	.318	.341	.363	.386	.409	.431	.454	.477	.499	.522	.545	.568	.591	.614	.636	.659	.682
136	.297	.320	.343	.366	.389	.412	.435	.458	.481	.503	.526	.549	.572	.595	.618	.641	.664	.687
137	.300	.323	.346	.369	.392	.415	.438	.461	.484	.507	.530	.553	.577	.600	.623	.646	.669	.692
138	.302	.325	.348	.372	.395	.418	.441	.464	.487	.510	.534	.557	.581	.604	.627	.651	.674	.697
139	.304	.327	.351	.374	.398	.421	.444	.468	.491	.514	.538	.561	.585	.609	.632	.656	.679	.703
140	.306	.330	.354	.377	.400	.424	.448	.472	.495	.518	.542	.565	.589	.613	.637	.660	.684	.708
141	.308	.332	.356	.380	.403	.427	.451	.475	.498	.522	.546	.570	.594	.618	.642	.665	.689	.713
142	.311	.334	.359	.382	.406	.430	.454	.478	.502	.526	.550	.574	.598	.622	.646	.670	.694	.718
143	.313	.337	.361	.385	.409	.433	.457	.482	.506	.530	.554	.578	.603	.627	.651	.675	.697	.723
144	.315	.340	.364	.388	.412	.436	.460	.485	.509	.533	.558	.582	.607	.631	.655	.680	.704	.729
145	.317	.342	.366	.391	.415	.440	.464	.488	.513	.537	.562	.586	.611	.636	.660	.685	.709	.734
146	.320	.344	.369	.393	.418	.443	.469	.492	.516	.541	.566	.590	.615	.640	.665	.690	.714	.739
147	.322	.347	.371	.396	.421	.446	.471	.495	.520	.545	.570	.594	.620	.645	.670	.694	.719	.744
148	.324	.349	.374	.399	.424	.449	.474	.499	.523	.548	.573	.598	.624	.649	.674	.699	.724	.749
149	.326	.352	.377	.402	.427	.452	.477	.502	.527	.552	.577	.603	.629	.654	.679	.704	.729	.754
150	.329	.354	.379	.404	.430	.455	.480	.506	.531	.556	.581	.607	.633	.658	.684	.709	.734	.759

MEASUREMENT OF TEMPERATURE
with the
BATHYTHERMOGRAPH (8)

The Bathythermograph (BT) Essential Parts



Origin. Woods Hole Oceanographic Institute, devised to determine the depth of wind mixing.

Mechanism.

Temperature Device. 45 feet of copper capillary tube operating a Bourdon tube.

Pressure (Depth) device. Sylphon bellows with slide carrier, Spring tension 320 lbs. compresses spring one inch; 450 ft. depth = 225 lbs. compresses spring 0.7 inches.

Recording device. A smoked glass slide is carried in an adapter fitted rigidly to the sylphon bellows, and moves with pressure on the long axis of the BT. A stylus fitted to the Bourdon tube moves with temperature on transverse axis.

The resultant motion is recorded by the scratch left by the stylus on the smoked glass slide.

Accuracy. A difference of 1/10°F. can be recognized in the temperature depth curve, if the instrument and slides are good. Normally 1/5°F. precision is expected and obtained. The absolute accuracy depends on the accuracy of the index observation.

Slides. Are smoked glass (1" x 1 3/4") made by moistening the glass with "skunk oil," and smoking in the yellow flame of an oil lamp.

Calibration grid. Each instrument is placed in a pressure tank and a series of calibrations made at known temperatures and pressures. This is amplified to show depths at 10 foot intervals, and temperature at 1°F. intervals. The instrument should be recalibrated every time an adjustment is made. Naval Research Establishment, H.M.C. Dockyard, Halifax, Woods Hole Oceanographic Institution at Woods Hole, Massachusetts, and Scripps Institution of Oceanography at La Jolla, California, are equipped to calibrate instruments.

Rigging.

The BT is secured to a sounding line (1/32" or 1/16" galvanized steel sounding line, or equivalent). The line is lead from a sounding machine (Kelvin) or suitable winch, over a travelling block on a boom leading well clear of the ship's sides.

Procedure.

(a) **Making the observation:** A glass slide is placed in the slide carrier, and the sleeve closed over the openings. This automatically brings the stylus against the slide. The line is hauled tight with the travelling block against the ship's side. Then the block is hauled out to the end of the boom while the line is slacked off to allow for movement. When the traveller is secure at the end of the boom, lower the BT to the surface and allow it to trail in the surface water for 30 seconds to come to temperature.

Let go at the winch and allow the line to run free till the required amount of line is run out, then stop the run out, and heave in. Bring the instrument to the block, then haul the block in board, at the same time taking up the slack in the line. Retrieve the instrument, and remove the slide. Handle only by the edges.

As soon as possible take a sample of surface water and observe the temperature, with a standard thermometer. (1) This provides a known point on temperature depth curve, by which the curve may be fitted to the calibration grid.

The wire-run-out depends on the ship's speed and the condition of the gear (how free it runs). Several trial runs should be made, noting the wire-run-out, on the measuring device of the winch, and the depth attained by the BT. These should plot in a smooth curve of the form

$$\left(\frac{\text{Wire out}}{\text{Depth attained}}\right)_{\text{Speed}} = K \quad \text{(constant)}$$

and for different speeds this takes the form

$$\frac{\text{Wire out}}{\text{Depth attained}} = e^{ks} \qquad s = \text{speed}$$

The temperature record may be examined at once by placing it over the standard grid in the viewer provided.

(b) Preserving the slide: First make index notations on the slide and dip it in fresh water, and finally in amyl acetate lacquer, and dry.

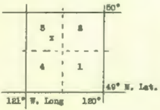
(c) Preserving records: It is customary to make the data permanent by a photographic enlargement of the slide, and its calibration grid, on the back of which all pertinent data is recorded.

(d) Auxiliary observations: (In data book against each observation)

Time — 2400 hour notation. Local standard or Greenwich Mean Time, note which. Then day/month/year by numbers in regular order from the shortest to longest time interval, e.g.

1521/23/5/46 = 3:21 P.M., 23rd of May, 1946

Position — Exact latitude and longitude to the degree of precision indicated by the navigation: i.e. this would be more precise in harbours than in the open sea.



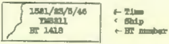
The unit squares of latitude and longitude are indexed by the bearings of the lowest numbered corner, and divided in quarters numbered as shown.

Exact position
Lat 49°41.2'N Long 120°37.8'W

Index
49120.3

<u>Weather</u>	Wind direction and force (Beaufort scale) Clouds (0-10). Barometer Air Temperature, <u>wet</u> and <u>dry</u> bulb.
<u>Sea</u>	Sea, and swell, Douglas scale. Surface water temperature.
<u>Index</u>	BT number (To indentify calibration grid) ship, observer, etc.

(e) <u>Notation on BT Slide.</u>

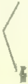


<u>Temperature Gradients.</u>

<u>Simple Gradients:</u>

/	Negative = Nan	(Temp. decreases with depth)
\	Positive = Peter	(Temp. increases with depth)
(	Changing = Charlie	(Gradient slight, subject to easy change; less than 0.5°F/100 ft.)
|	Mixed or Isothermal = Mike	(Temp. constant with depth)

<u>Complex Gradients:</u>



etc.

Significance.

Isothermal	indicates water has been mixed turbulently, either by the wind, or flow thru channels, etc.
Negative	indicates surface heating; insolation.
Positive	indicates surface cooling exceeds insolation and convection. Convection may be repressed because of salinity gradient, and in this case the positive gradient is stable.
Charlie	indicates unstable situation subject to diurnal or tidal change. For example Afternoon effect. This is the surface warming (0-1°F) of the surface 10 to 15 feet during the day, and subsequent cooling during the night. Occurs only in clear weather, with light winds, during the summer.

Interpretation

Structure of water mass.

Structure is the relation of density to depth, at any one position, at a specified time. Obviously it may change with the distance or time. In any case it may be resolved into a temperature and salinity factors.

It may be generally accepted (on the basis of experience) that any major discontinuity in the structure will be indicated in the temperature gradient. (Note: gradient implies relation to depth unless otherwise specified.)

Depths 0
1 and multiples
2
4
6
10

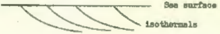
Heretofore it has been customary (not having any previous knowledge of the structure of the water mass) to make observations of temperature and salinity (etc.) at a series of standard intervals, and to interpolate between these data.

The BT offers a means of making a quick estimate of the structure of the water mass, and if spot observations are to be taken, a means of arranging these to obtain the maximum of information from a minimum number of samples.

For example in the BT records indicated situation (1) would require at least six specific observations, while situation (2) could be analyzed with (3) observations.

Not only does the BT data provide the necessary foreknowledge of the situation necessary for intelligent (as opposed to blind) observation, but prevents overlooking anomalous situations such as the temperature inversion in situation (1).

An application of this technique occurs in the observation of Upwelling.



By taking a series of BT in a line offshore the change in the structure with distance can be readily observed.

Also internal waves may be accurately observed by taking a time series of BT's at one position, and noting the rise and fall of some demarcation point on successive slides.

References.

Instructions for the Care and Use of the Surface Vessel Bathythermograph.
Navships 943-42. Bureau of Ships, Washington, D.C.

Instructions to Marine Meteorological Observers. Circular M. June 1941,
U.S. Dept. of Commerce, Weather Bureau, Washington, D.C.

NOTES ON TAKING WATER TEMPERATURES (4)

Knowledge of the temperature of the surface sea is of increasing interest to fishermen on the Pacific Coast of Canada. Adoption of a standard method of obtaining temperatures will make individual readings comparable to the temperatures reported in these Progress Reports and elsewhere.

Type of Instrument

Experience has shown that mercury thermometers are the most reliable. The ideal type is one which has the graduations engraved on the glass stem, and which is mounted in a protective metal case that has a small well around the bulb. Recently improved makes of mercury thermometers reflect the mercury column as a red band, or as a black band on a yellow background. These types are very easy to read.

The thermometer can be graduated in either the Centigrade or Fahrenheit scale. The scale should cover a temperature range from 32°F. (0°C.) to 85°F. (20°C.) and the graduations should be in half degrees, certainly not any larger than one-degree intervals. A one-degree division that is smaller than one-eighth inch makes it difficult to estimate fractions of degrees. The more common types of chemical thermometers have scale ranges of -10° to 110°C. or -30° to 120°F., with one-degree intervals. These are quite satisfactory for observing water temperatures, and are obtainable from scientific supply houses and marine equipment stores.

The unprotected glass stem of a chemical thermometer is quite fragile, and it is advisable to protect it with a metal shield. The cost of an armour for a thermometer is small compared with the original cost of the instrument, and is good insurance against loss by breakage. It is good policy to have a spare thermometer on hand to ensure the continuity of the temperature records.

There are numerous types of thermometers that are mounted on wooden or metal backs. This provides a fair protection to the glass stem, but usually the scale is on the backing and not etched on the stem. Consequently, if the glass stem slips or moves in the clamps it no longer bears a proper relation to the scale graduations, and the readings will be wrong. Therefore it is important that the scale be etched in the glass stem of the thermometer.

Care of Thermometers

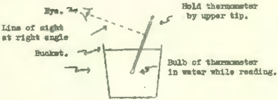
When not in frequent use the thermometer should be placed in a wooden case, stored in an upright position with the bulb down, and kept in a cool place. When the thermometer is being used on deck (and we hope it will be in a protective case) it should be attached to one end of a strong line which has its other end secured inboard. The best plan is to place the thermometer in a box attached to the inside of the bulwark and protect it from the direct heat of the sun.

This is important with instruments that do not read very high (under 100°F, or 38°C,) because the expanding mercury might burst the instrument.

The thermometer should be kept free of grease so that no drops of water will adhere where the reading might occur and thus make it difficult to observe.

Taking the Water Temperature

The best method of obtaining a surface water temperature is to cast a bucket over the side of the boat, fill it with water, and then haul it up and set it on the deck where it is sheltered from the wind and sun. Immerse the whole thermometer in the bucket immediately. If the thermometer is an unprotected glass stem, leave it immersed for one minute. If it has any type of metal shield or backing, leave it for two minutes. During any longer period of time the water in the bucket may cool or warm appreciably. Lift the thermometer out of the water by its top only far enough to see the mercury column (see illustration). Never hold the thermometer below the top of the mercury column. Leave as much of the glass stem and bulb in the water as is possible. These precautions prevent the reading from changing while it is found on the scale. Hold the thermometer at right angles to the line of sight and take the reading. The temperature should be recorded immediately after it is read. A "remembered" reading is not always correct.



Water temperature readings can be taken from the thermometer on the engine room intake, but there are many reasons why these might be incorrect. For instance, engine room intake thermometers are not usually very accurate, and quite often they are graduated only in two-degree intervals. Also, the intake water is not drawn from the sea surface, and it could be warmed while passing through the engine room to the intake thermometer. If readings are taken on an intake thermometer they should always be checked once a day against a bucket temperature reading taken at the same time, and then corrected.

Temperatures are converted from one scale to another using whichever of the following formulae is appropriate:

$$°\text{F.} = (1.8 \times °\text{C.}) + 32 \quad \text{or} \quad °\text{C.} = \frac{°\text{F.} - 32}{1.8}$$

Thermometer Errors

Any thermometer may have a difference between the reading as seen on the scale and the true temperature. In good instruments the error is small and negligible, but in cheaper thermometers it might make a big difference in the readings.

To determine the error, completely immerse the thermometer (without its protective casing) in a bucket full of pure, crushed, salt-free ice. Flake ice is suitable and easily obtained. The ice should be melting, and the resulting mixture of ice and water should be continually stirred. This temperature is always 32°F. or 0°C. Withdraw the thermometer, holding it by the top, until you can see the top of the mercury column. The difference from 32°F. is the error of the instrument, and should be applied to all readings. If the reading is higher than 32°F. then the amount by which it exceeds 32°F. is to be subtracted from the temperature readings; if it is lower than 32°F. then the error is added to the readings. It is advisable to make a note of this correction in the log book of temperature observations.

Damaged Thermometers

It frequently occurs that the column of mercury in a thermometer becomes separated. This is not always a defect in manufacturing. A simple method of uniting the broken column is to fasten the thermometer in its case securely to an engine room bulkhead, where it is cool and vibrating, and leave it there for several days. Failing this, there are several methods generally used by laboratory workers which require more careful technique. (1) Try cooling the bulb of the thermometer by immersing it in an ice-salt mixture, thus drawing the entire mercury column into the bulb. Remove the bulb from the cooling mixture, allow it to warm slowly in the room air, and the column will usually reunite. Try this method several times. (2) Sometimes a separated column may be united by warming the bulb gently over a low heat. Move the thermometer back and forth slowly and the mercury will be forced gradually into the expansion chamber at the top. As the thermometer cools while held in a vertical position, the column should recede united. This method is not so safe as the first one, and extreme care should be taken to avoid filling the expansion chamber completely with mercury.

H.J. Hollister

From Progress Reports of the Pacific Coast Stations of the Fisheries Research Board of Canada, No. 78, April, 1949, pp. 14-16.

CALCULATION OF ACTUAL DEPTH (1, 2)

In the process of sampling, the reading of the meter wheel which records the length of cable played out, can not be generally taken as the actual depth from which the samples were procured. In other words, it can not be assumed that the cable is suspended exactly perpendicularly from the boat. Currents and wind will cause a drift, and the cable will follow the course of a curved line. To ascertain the actual depth, an unprotected reversing thermometer is utilized. From the reading of this thermometer, the reading of the protected thermometer and the chemical determinations for chlorinity, it is possible to calculate the actual depth at which samples are taken, providing the pressure constant of the unprotected thermometer is known.

The protected thermometer is so constructed that the bulb of the main thermometer is not affected by pressure. However, with the unprotected thermometer, the pressure acts on the thermometer bulb, forcing much more mercury into the capillary than by thermal effects alone. Thus a difference between the reading of the two thermometers gives a measure from which the depth may be calculated.

The correction of the unprotected thermometer which is used in conjunction with the protected thermometer, is simpler of calculation because the temperature of reversal of the latter is known. The correction is determined from

$$\Delta T = \frac{(Tw - t)\ (T' + V_o)}{K} + I$$

Tw = Temperature of reversal of the protected thermometer.
t = " " the auxiliary thermometer of the unprotected thermometer.
T' = Reading of the unprotected thermometer.
V_o = Degree volume of the unprotected thermometer.
K = 6100
I = Index correction.

From the corrected readings of the protected and unprotected thermometers, the depth at their reversal may be computed from the equation

$$D = \frac{(Tu - T)}{Qd}$$

where D = Depth in meters.
Tu = Corrected reading of unprotected thermometer.
T = " " " protected "

Q = Pressure-constant of the unprotected thermometer,
d = Mean specific gravity of the water column above the thermometer and is obtained from the chlorinity determinations and the temperatures.

The pressure constant of the unprotected thermometer is the change in degrees in corrected reading caused by a change in pressure of 0.10 kilograms per square centimeter. The constant is of the order of magnitude of 0.01 and is ascertained from the thermometer certificate which, however, usually gives the degree change in ten times the value of Q, or in other words, the degrees change in readings per kilogram per square centimeter change in pressure. In general, one meter in depth in equivalent to a change 0.01°C. for the corrected readings.

<u>Illustration</u>: The corrected reading of the protected thermometer is 1.95°; of the unprotected thermometer 39.82°; the average density of the water, computed from chlorinity and temperature determinations made at twelve different depths is 1.02550. The pressure constant as kilogram per square centimeter, is given as 0.1144. The true depth is

$$D = \frac{39.82 - 1.95}{.01144 \text{ x } 1.02550} = \frac{37.87}{.01173} = 3228 \text{ meters}$$

OCEANOGRAPHIC DATA (4, 8)

Oceanographic data must be processed from the stage of original records, to corrected data, to analytical form, and final presentation. Data is rarely, if ever, presented in its original form, which must be corrected for the characteristics of the instruments and standards, and usually interpreted to suit the requirements of the project.

Records

There are no set forms or sequence for records, but they must be durable, convenient, and show all steps of development. It has been found most practical to enter original data, and to make instrument and standard corrections and preliminary conversions on an "original data sheet". From this the corrected values are transferred to a "fair sheet" which is the record of the oceanographic properties in accepted units. Further processing may be required to fulfill the requirements of an investigation.

Original Data Sheets

The original records are the primae facie evidence of the observation and every care must be taken to ensure their reliability, permanence, and security. To these ends certain rules should be followed.

1. Data sheets are mimeographed forms on a good grade of bond paper that is durable, and usable when wet. Space is provided for the conversion of observed values (titer, thermometer readings, column heights, etc.) to the corrected values (S°/oo, T°C, concentration, etc.).

These sheets must provide for all pertinent data, factors, and references, defining the conditions of the analyses. A type of form frequently used for surveys where temperature, and salinity is observed is shown in figure 1.

When several analyses of the water sample are to be made it is convenient to have separate "original data sheets" for each analyst.

2. The original data are entered in duplicate. Two data sheets with a carbon interleaf are provided for each station, and are secured in a spring clipped hard cover. The cover should be heavy enough that it cannot be blown overboard by wind, or washed out the scuppers.

3. Entries are made with soft (B or HB) black lead pencil. Ink or indelible pencil records smear on wet paper, and fade with time. The long history of exploration has proven the efficacy of soft black lead pencil records.

4. No erasures are made on the original data sheets. If a number is to be changed, it is crossed out and the new number entered above it.

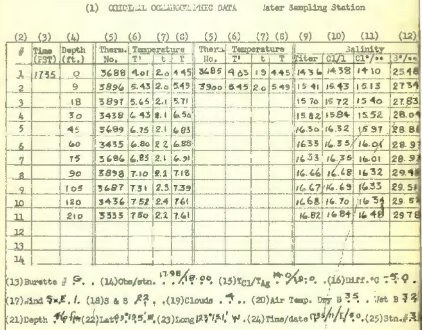
5. When entries are complete, the data sheets are separated and clamped in separate filing folders, from which they are never removed.

6. The original data sheets remain with the expedition, while the duplicates are sent, by registered mail, to the home establishment at the first opportunity. It was this precaution which preserved the records of Captain Cook's explorations.

7. It is customary to observe the properties of the water at a series of discrete depths, at a position, at a fixed time. Such a series is termed a station, and provides a unit of data requiring individual treatment. It may be a water sampling station, bathythermograph (BT) station, etc.

8. It has been found advisable to record the actual readings of the instruments, and subsequently to make the corrections. This preserves the original observations, which cannot be repeated, and permits checking all subsequent transformation steps.

It has been found that attempts to make mental corrections at the time of observation invariably results in error in the records, and confusion as to the corrections made. The observer is busy enough with essential considerations without the complications of mental arithmetic.



(1) OFFICIAL OCEANOGRAPHIC DATA Water Sampling Station

(2)	(3)	(4)	(5)	(6)	(7)	(8)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
#	Time (PST)	Depth (ft.)	Therm. No.	Temperature			Therm. No.	Temperature			Salinity			
				T'	t	T		T'	t	T	Titer	Cl/l	Cl°/°°	S°/°°
1	1735	0	3688	4.01	2.0	4.45	3685	4.63	1.9	4.45	14.36	14.38	14.10	25.4
2		9	3896	5.43	2.0	5.49	3900	5.45	2.0	5.49	15.41	15.43	15.13	27.34
3		18	3897	5.65	2.1	5.71					15.70	15.72	15.40	27.83
4		30	3438	6.43	2.1	6.50					15.82	15.84	15.52	28.0
5		45	3689	6.75	2.1	6.83					16.30	16.32	15.97	28.8
6		60	3435	6.80	2.2	6.88					16.33	16.35	16.01	28.9
7		75	3686	6.83	2.1	6.91					16.33	16.35	16.01	28.9
8		90	3898	7.10	2.2	7.18					16.66	16.68	16.32	29.4
9		105	3687	7.31	2.3	7.39					16.67	16.69	16.33	29.5
10		120	3436	7.52	2.4	7.61					16.68	16.70	16.34	29.5
11		210	3333	7.50	2.2	7.61					16.82	16.84	16.48	29.7
12														
13														
14														

(13) Burette # G. . (14) Obs/stn. 17.98/18.00 (15) T_{Cl}/T_{Ag} 18.0/18.0 . (16) Diff. °C 5.0 .

(17) Wind SxE, 1. (18) S & S 2 . . (19) Clouds 4 . . (20) Air Temp. Dry B 35 . Wet B 32

(21) Depth 46 fm (22) Lat 49°19.5' N. (23) Long 123°15.1' W. (24) Time/date 1735/11/1/50. (25) Stn.# 3

Figure 1

Explanation of Original Data Sheet

Line 1	Title: The home address should be printed here or on the reverse of the sheet, so that the data may be identified.
Column 2	Number of sample in the station. This refers to the number of the water sample bottle.
Column 3	Time The time of observation to the nearest minute in local standard time is recorded for each sample in the station. The entry is made in 24 hour notation (1835 = 6:35 p.m.; 0635 = 6:35 a.m.). This time refers to the instant of dropping the messenger at a water sampling station, or casting the bathythermograph at a BT station. Some organizations require Greenwich Civil (mean)time, but it has been found that the transformation is more correctly made at leisure,than during the bustle of station observing.
Column 4	Depth refers to the depth from which the sample was taken. Oceanographic observations are made in terms of several units of depth (meters, feet, yards, fathoms) wherefore it is essential that the units be specified.
Column 5	Thermometer number. It is presumed that the characteristics and standardization of the reversing thermometers are recorded and indexed by their serial numbers in the home laboratory and on board ship so that this index is all that is required.
Column 6	Temperature observed on the main thermometer (T') to the the degree of accuracy required (e.g. ± 0.01 °C).
Column 7	Temperature observed on the auxiliary thermometer (t) (± 0.1 °C).
Column 8	True temperature in situ (T). This quantity is computed from the data expressed or implied in columns 5, 6, and 7 according to the procedure outlined in the section on Measurement of Temperature.
Column 9	Titer of the sea water sample obtained as described in the section on the Determination of the Chlorinity of Sea Water.
Column 10	Chlorosity of the sea water sample including burette, standard solution, and temperature corrections.
Column 11	Chlorinity of the sample determined from the chlorosity by table I of the previous reference.
Column 12	Salinity of the sample evaluated from the chlorinity by inspection of Knudsen's tables or by the formula in the previous reference.

Item 13 Burette number. This identifies the burette and its scale corrections which are presumably available in the home laboratory and on board ship.

Item 14 Obs/stan. The observed titer of the standard sea water / and the theoretical titer of the standard sea water. These data are required for the solution corrections as outlined in the previous reference.

Item 15 T_{Cl}/T_{Ag} Temperature of the sea water sample / and temperature of the silver nitrate solution.

Item 16 Diff.°C Temperature difference T_{Cl} - T_{Ag} which is required to select the proper column for the conversion Cl/l to Cl°/oo in Table I of the previous reference.

Usually the samples from one station are analysed in a single operation, and this temperature relation is constant. However it should be checked frequently and significant differences noted.

Item 17 Wind Direction from which the wind is blowing and estimated force on the Beaufort scale (cf. Instructions to Marine Meteorological Observers, Circular M, U.S. Department of Commerce, Weather Bureau, Washington D.C., 1941, Superintendent of Documents, Washington D.C.; 25 cents).

Item 18 S & S. Sea and swell according to the Douglas sea and swell scale (cf. previous reference).

Item 19 Clouds Proportion of sky (tenths) covered by clouds (cf. previous reference).

Item 20 Air Temp. Air temperature as observed on the dry and wet bulb thermometers (cf. previous reference).

Item 21 Depth of water at the station from lead line or echo sounding. This is required to estimate the proportion of the water column examined in the above data.

Item 22 & 23 Position The latitude and longitude of positions at sea are observed and recorded to the nearest 2% of the distance from the shore.

In the sea-going operations it is customary to rely on the ship's officers for navigation and position. For this purpose a deck log is provided (figure 2).showing the pertinent date for reproduction of the navigation between stations. The position must be entered on the original data sheet as soon as practical, to complete the record. Data at an unknown position is of no value.

Item 24 Time/date group. This is the time of sample number 1 and the date in local standard time.

Because of the confusion that results from the order of numerical notations by the British system (1130/6/8/50 = 11:30 a.m., 6 August, 1950) and the American system (1130/6/8/50 = 11:30 a.m. June 8, 1950) it is advisable to distinguish between the notation for day and month, e.g. 1130/6/VIII/50 or better 1130/6 Aug./50. The time group is always four figures and cannot be confused with the others which are always two figures.

Other Properties and Constituents

Similar types of original data sheets may be provided for observations of other properties and constituents as required. In all cases the observed measurements, standards, etc. are noted on the original data sheets, and subsequently transformed to the units in which they are to be reported each step and factor being shown.

Fair Data Sheets

The data from each station are accumulated on a fair data sheet in the required units. These sheets are usually bound in a looseleaf note book for easy manipulation.

Index

It may be noted that the time date group forms a convenient index for oceanographic stations e.g. 1215/3/VIII/50; time/day/month/year. Alternatively the position index is frequently used as outlined in the section on bathythermograph data. 49 124 (3); latitude 49° longitude 124° quarter 3, with a sub index showing the exact position. Frequently data are indexed under both systems to facilitate sorting in terms of time or position.

DECK LOG

Depth. 8 fms. Sample taken (time) 1701 Proceed 1704

Course 303° at 8.5 knots.

---

(1) Station 32 (2) Date 11/I/50 (12) Wind SE 1 (13) Temp. 35°D 33°W

(3) Stop (time) 1728 (14) Sea 22 (15) Bar. 1009.8

(4) Observe position (time) 1730 Weather S-4

(5) Position (6) Lat. 49° 19.5' N

Pt. Atkinson 308°T (7) Long. 123° 15.1' W

Spanish Bank Bouy 194°T

(8) Depth 46 fms (9) Samples taken (time) 1735 (10) Proceed 1742

(11) Course and speed 270° at 8.5 kts.

Station 33 Date 11/I/50 Wind N-4 Temp. 30°D 28°W

Stop (time) 1844 Sea 21 Bar 1006.0

Figure 2

Explanation of Deck Log

The Deck Log is normally kept on the bridge of the ship and entered by the officer of the watch. It is independent of the Original Data Sheet and every care must be exercised to ensure that the cross references are consistent between the two. It is most satisfactory to refer all data to local standard time as carried by the ship's clock.

(1) Station number or designation. This is usually committed during the operation, and entered when a reference key is assigned.

(2) Date in local standard time.

(3) Stop (time) The time the ship is stopped.

(4) Observe position (time). The time required to observe a station varies from twenty minutes to twenty hours, and position may be observed at any time during the stop. When the ship is drifting it is frequently necessary to know the time to which the logged position refers.

(5) Position. This is the description of the position in terms of the method of observation, e.g. it may be bearing and distance from a mark, three point bearings by compass or sextant, or astral intercepts.

It is advantageous and usually necessary to plot the position of each station on a suitable chart at the time of observation. This chart is the original record of the navigation and should be preserved as the original record. It is advisable to provide ample copies of the charts required, and to "ink in" the plot with waterproof ink before filing.

(6) and (7) Latitude and longitude determined from item (5) and the plot on the chart. These values are repeated on all original data sheets and subsequent recordings.

(8) Depth of water at the station from log line or echo sounding.

(9) Samples take (time) The time of dropping the messenger to trip the water sampling bottles. If there are two casts this time refers to the second.

Comparison of this time with time of observation of position (item 4) indicates the reliability of the position. These items should be made to coincide as nearly as possible.

(10) Proceed The time when the ship proceeds on the course to the next station.

(11) Course and speed to the next station, every change of course and speed with the time of alteration should be noted so that the dead reckoning may be reproduced.

(12) Wind direction and force, cf. Instructions to Marine Meteorological Observers, Weather Bureau Washington, D.C. (Superintendent of Documents, Washington D.C.; 25 cents).

(13) Temperature of the air on the dry and wet bulb thermometer, cf. previous reference.

(14) Sea & Swell cf. previous reference.

(15) Barometer reading corrected for reference errors. cf. previous reference.

The Deck Log and original track charts are part of the original data to be collected by the Oceanographer and preserved for reference.

TABLE I

Element determined as:-	Factor for conversion from weight per unit volume to weight-atoms per same volume
mg. liter	**mg. atoms liter**
$\underline{O}$ or $\underline{O}_2$	0.06250
$\underline{P}$	0.03228
$\underline{P}_2O_3$	0.01818
$\underline{P}_2O_5$	0.01408
$H\underline{P}O_3$	0.01250
$H_3\underline{P}O_4$	0.01020
$(\underline{P}O_4)^{-}$	0.01052
$\underline{N}$ or $\underline{N}_2$	0.07139
$\underline{N}_2O_3$	0.02631
$\underline{N}_2O_5$	0.01852
$H\underline{N}O_2$	0.02127
$H\underline{N}O_3$	0.01587
$(\underline{N}O_2)^{-}$	0.02174
$(\underline{N}O_3)^{-}$	0.01613
$\underline{N}H_3$	0.05871
$(\underline{N}H_4)^{+}$	0.05543
$\underline{N}H_4OH$	0.02853
$\underline{Si}$	0.03564
$\underline{Si}O_2$	0.01665
$(\underline{SiO_3})^{=}$	0.01315
$\underline{C}$	0.08333
$\underline{C}O_2$	0.02273
$(H\underline{C}O_3)^{-}$	0.01639
$H_2\underline{C}O_3$	0.01612
$(\underline{C}O_3)^{=}$	0.01667

Standard Units (8)

It was agreed at the 5th Pacific Science Congress (1933) in Vancouver, Canada that, "The constituents of sea water be expressed as milligram-atoms of the identifying element, (C, N, O, I, etc.) per kilogram of sea water, and that the general chemical nature of the sea as a function of its physical properties be expressed as chlorinity."

Formerly the concentration of the constituents in sea water were expressed in grams, or milligrams per liter, or cubic meter. The factors for conversion from one system of units to the other are given in Table I.

The analyses are made as milligrams or mg. atoms per liter; this value divided by the specific gravity in situ (σ_t) yields the concentration as mg. atoms per kilogram. The latter value is from one to three percent larger than the former, and correction is usually less than the error of determination of the minor constituents (O_2, P, N, Si, etc.) and is usually neglected. In this case the results are reported as mg. atoms per liter.

Some constituents are more conveniently expressed in alternative units:-

Dissolved oxygen is reported as milligram atoms per kilogram of sea water, and as the proportion of the solubility (saturation) at normal atmospheric pressure (760 mm. mercury) under the conditions of temperature and chlorinity existing in situ, according to the tables of Whipple and Whipple. (Solubility of oxygen in sea water, J. Amer. Chem. Soc. 33, 362, 1911) (cf. Section on Determination of Dissolved Oxygen in Fresh and Seawater).

Hydrogren ion concentration is reported as

$$pH = \log_{10}\frac{1}{[H^+]} = -\log_{10}[H^+]$$

Turbidity is reported as the number of milligrams of silica (precipitated Fullers earth prepared to pass a 200 mesh sieve) per liter of sea water that would give the same optical interference effect during colorimetry (A. P. H. A. pp 4) (Standard Methods of Chemical Analyses - Scott, pp. 1410).

Natural Color is reported as the mg. of platium contained in a colorimetrically matched standard solution of equal volume. The standard solution of designated color 500 contains:

1.246 grams potassium platinic chloride ($PtCl_4KCl$)
(contains 500 mg. Pt)

1.0 grams crystalized cobalt chloride ($CoCl_2.6H_2O$)
(contains 250 mg. Co)

100 ml. hydrochloric acid (HCl)

made up to one liter.

(Standard Methods of Chemical Analyses - Scott pp. 1410)

Presentation of Data

Data obtained in the course of oceanographical investigations may be presented in tabular or graphical form. Tables have the advantage of listing the data compactly, and with greater precision than would be possible on graphs of the same size, but do not "picture" the data. Graphs provide interpolation between the points, emphasize the continuity, and are readily comparable. Recent studies indicate that the graphical interpolations of temperature and salinity structure are probably more representative than arithmetic interpolation between tabular points.

The concepts of tables and graphs are interchangeable, the former being favored in publication, where space is at a premium, and the latter in the analyses of data where manipulative properties are of more value.

One dimensional graphs

The orthagonal, one dimensional graph on a natural scale is the simplest form, and is the only one amenable to quantitative analyses. In such a graph the measure of a single property of the water (salinity, temperature, etc.) is plotted as a function of one dimension (time, depth, distance, etc.) and all other functions are ignored. In this form of graph the slope (differential) and the area (integral) may be determined directly, and is therefore preferable for analyses to tabular data where these operations imply tedious arithmetical procedures.

The one dimensional graphs provided by most recording instruments (bathythermograph, etc.) are radial to some degree, and frequently have functional scales (e.g. logarithmic or hyperbolic). These graphs are of interest only as a continuous record of the relation, and must be transformed to orthagonal axes and natural scale for analyses.

Interpolation

There are several instruments to provide continuous records of temperature, and pH, with time, which may be manipulated to represent distance or depth. The bathythermograph is the only oceanographic instrument that provides a satisfactory record of a property (temperature) with a linear dimension (depth). There is considerable research directed towards recording salinometers, but little or no interest in continuous recordings of other properties.

It follows that graphs of all properties of seawater (except BT slides) require interpolation between the data observed at discrete intervals. This process implies appreciation of the structure of the sea, and since this is the conclusion usually being sought, it would appear that progress in oceanography is dependent on advances in instrumentation. This is partially true, but some rules can be advanced to aid interpolation.

Recent researches have shown that the temperature, salinity, and density distribution in each depth zone tend to be linear functions of the logarithm of depth. In this plot the relations are straight lines. The general procedure in to plot the data on logarithmic graph paper setting the surface observation at 0.1 meter, or 1 foot, and connecting the points by the fewest possible straight lines. These curves are then transformed to natural scales, and the necessary operations completed.

Two dimensional graphs

Constant values (isometers) of an oceanographic property may be plotted as a function of two dimensions. The position of the isometer with references to one dimension is usually determined from the one dimensional graph, and plotted with reference to the second dimension on the abscissa or ordinate corresponding to the position, or time of observation. Such graphs include contour maps and charts, cross sections, and time charts. They illustrate the continuity of the property in the two dimensional system, and are not amenable to precise analyses or direct operation.

Excerpts from "Instructions to Marine Meteorological Observers"
U.S. Dept. of Commerce, Weather Bureau,
Circular M - 7th Ed. - June, 1941

WIND

Wind Direction - The direction of the wind to be recorded is the true direction, not the magnetic. Its direction as given by the compass should, therefore, be corrected for the magnetic variation and for the deviation, if this is large, as is sometimes the case.

The direction of the wind is best ascertained by making use of the fact that the crest lines of the smallest ripples on the sea surface are perpendicular to the direction of the wind. These ripples as every seaman knows, are very sensitive to sudden changes in the character of the wind. Accentuation of them by a localised increase in wind velocity produces an apparent darkening of the sea surface, which serves to show the rate of travel of individual gusts or puffs. With wind forces of 6 (Beaufort) or more the wind direction may also be correctly estimated from the direction of the streaks of foam which are then formed.

Occasionally the observer is confronted by a peculiar problem when making an observation. If a squall happens to pass over the ship just at the time of observation the direction of the wind may suddenly change by an appreciable amount. The observer may not be able to tell whether the change represents a definite and widespread shift or simply a local disturbance, after the passage of which the wind will revert to the direction it had maintained prior to the squall. If he believes that it represents a local and temporary condition, he may think it proper to record the wind direction which had prevailed before the squall. The correct procedure in such a scase is as follows: Record the wind direction that happens to be prevailing at the moment of observation, even if it may appear to be only temporary.

Observers sometimes fail to distinguish between shifting winds and variable winds. The term "shifting" applies to winds whose direction is changing in accordance with the movement or development of some well-marked cyclonic or anticyclonic system. The term "variable" applies to weak winds (force 3 or less) whose direction is indefinite, coming in feeble puffs, first from one point, then from another. The term "variable" should be applied also to the strong but short-lived winds which are associated with local squalls.

Wind force - To an experienced observer the appearance of the sea surface serves as the best means of estimating the true wind force, just as it affords the best means of ascertaining correctly the wind direction. However, the appearance and the roughness of the sea obviously depend upon a number of factors, and not solely on the strength of the wind locally. The length of time the wind has been blowing and the rate at which it is changing its direction and velocity are some of the more important influences. Consequently it is virtually impossible to lay down reliable criteria which will be valid at all times; a precise knowledge of the relation of wind force to the appearance of the sea must be gained by experience.

In recording the force of the wind, the scale devised by Admiral Sir Francis Beaufort is employed. According to this scale, which is contained in the code table below, the wind varies from 0, a calm, to 12, a hurricane, rated as the highest force ever attained.

Assuming that the ship is in the open sea where there is an absence of appreciable current, and that the wind direction and force have remained essentially constant for a sufficient length of time so that the sea surface is in equilibrium, so to speak, with the wind, the following conditions usually are observed. With force 0 (calm) the surface of the sea is glassy; with force 1 the sea tends to be rippled in patches. With force 2 the entire surface of the sea is rippled and miniature waves several inches in height are formed. One of the principal distinctions between force 1 and force 2 is afforded by the distinctness with which the sea horizon may be seen on clear days. With force 1 the horizon presents an indefinite line, whereas with force 2 the horizon is quite sharply delineated. A wind force of 3 produces a definite wave formation with scattered incipient whitecaps making their appearance. Force 4 is characterized by numerous well-developed whitecaps, which give the ocean a spotted appearance. Force 4 produces a distinct sea which is easily distinguished from any swell that may be prevailing. The difference in the appearance of the ocean surface between forces 4 and 5 is principally one of degree. However, with force 5 spume tends to be blown from the breaking wave crests, whereas no such tendency is noticeable with force 4. No attempt will be made here to describe the appearance of the sea surface with winds of greater strength, because these occur usually in the neighborhood of cyclonic storm centers where the rapid changes of direction and velocity do not permit the sea to reach a state of equilibrium with respect to the wind at any given time.

The motion of the air is never perfectly uniform, but is subject to incessant variations in direction and velocity. These variations are designated at "turbulence" or "gustiness". The occurrence of unusual gustiness should always be noted in the weather report. It should not be reported by describing the state of weather as "squally". Gusts are distinguished from squalls by their brief duration, by the absence of any special accompanying cloud formation and by the fact that the wind does not vary appreciably from its average direction. Unusual gustiness may be defined as the condition prevailing when the wind temporarily exceeds its average force by a full figure or more on the Beaufort scale but continues essentially (i.e., to within two points) from the same direction. Care should be taken that the average force of the wind is recorded, and not its force during the gusts.

STATE OF WEATHER

b. - Blue sky, cloudless
bc - Blue sky with detached clouds
c. - Sky mainly cloudy
d. - Drizzling, or light rain
e. - Wet air, without rain
f. - Fog, or foggy weather
g. - Gloomy, or dark, stormy-looking
h. - Hail
l. - Lightning
m. - Misty weather
o. - Overcast
p. - Passing showers of rain
q. - Squally weather
r. - Rainy weather, or continuous rain
s. - Snow, snowy weather, or snow falling
t. - Thunder
u. - Ugly appearance, or threatening weather
v. - Variable weather
w. - Wet, or heavy dew
z. - Hazy weather

To indicate great intensity of any feature, its symbol may be underlined; thus: r., heavy rain.

CLOUDS

Amount of clouds - The proportion of the sky covered by clouds, irrespective of type, should be recorded for total amount according to the scale 0 to 10. In this scale 0 represents a sky that is cloudless at the time of observation, 1 a sky that is less than one-tenth covered, and so on to 10, which represents a sky completely overcast. The amount of clouds should agree in general with the state of weather; that is, a sky with less than one-tenth cloudy covering is clear, 1 to 5 tenths is partly cloudy, 6 to 9 tenths is cloudy, 10 tenths is overcast.

In the thin types of "mackerel" clouds there are almost always gaps or spaces through which clear sky can be seen. When these conditions prevail, therefore, the amount of cloud should never be recorded as greater than 9, even though such clouds are spread all over the sky.

In case the sky is completely obscured by dense fog, it should be described as overcast, and ten-tenths of dense fog, without direction of movement, should be entered in the space for cloud amount. However, should the ship be enveloped in fog (or haze) which allows blue sky, sun, moon, or stars to appear through and there is no trace of cloud above the fog (or haze), the cloud amount should be recorded as 0. On the other hand, if clouds are visible above the fog, an attempt should be made to estimate the total amount of cloud, and this should be recorded as though no fog were present.

SEA AND SWELL

When a light wind blows over a water surface it produces at first a series of ripples, moving with the wind. As the ripplies move forward with the wind they increase in size. A strong wind produces larger waves, and if it continues, a heavy sea results.

After a wave moves beyond the influence of the winds which caused it there is a change in its form. The most rapid change at first is a decrease in height. Finally the wave becomes a relatively low, undulating movement of the sea surface, known as a swell. In recording observations in accordance with the following scales, swell is wave motion produced by winds at some distance from the point of observation.

The swell is distinguished by two features; first, its relatively smooth, undulating form, without the steep and ragged crests characteristic of waves actively driven by local winds and, second, the movement of winds and waves in difference directions, indicating that the waves have been formed elsewhere by winds from another quarter. Ordinarily, then, waves which are moving with the wind constitute the "sea" while a relatively low, undulating sea surface, with motion in a direction different from the local wind, is the "swell".

These definitions are not entirely satisfactory. Usually, the ocean surface is disturbed by both forms of wave motion, with the swell from distant winds crossing the local sea. The combined effect is the "sea", while the well-defined ridges of waves moving in a different direction from the local wind are the "swells".

State of sea - The following scale should be used in classifying the character of the sea disturbance. In recording observation in accordance with this scale, "sea" may be considered to be composed of swells, combined with waves produced by the winds at the place of observation.

State of Sea

Scale	Description	Height of wave crest to trough
0	Calm	0
1	Smooth	Less than 1 foot
2	Slight	1 to 3 feet
3	Moderate	3 to 5 feet
4	Rough	5 to 8 feet
5	Very rough	8 to 12 feet
6	High	12 to 20 feet
7	Very high	20 to 40 feet
8	Precipitous	Over 40 feet
9	Confused	

The scale of sea disturbance is approximate, based roughly on the observer's judgement as to the height of waves. Accurate estimates of wave height are not easily made on shipboard. For large waves, with the ship on an even keel in the trough of the wave, the observer's height above the water line where he sees the crest of the wave coincide with the horizon, is taken as the height of the wave.

Character of swell

Scale	Description	Scale	Description
0	No swell	5	Moderate swell, long
1	Low swell, short or average length	6	Heavy swell, short
2	Low swell, long	7	Heavy swell, average
3	Moderate swell, short	8	
4	Moderate swell, average length	9	

Period of swells - Observations of length and height of the swell are not so valuable as the period. The number of swells that pass a given point in one minute may be taken as the period. On shipboard this may be calculated by watching the rise and fall of a patch of foam and noting the time interval.

In so doing, rise and fall due to the true swell, and not the smaller waves, should be noted. A series of such observations will give a good approximation of the time interval in seconds or the period expressed in number of swells in a minute.

BEAUFORT SCALE FOR WIND

Beaufort Number	General Description of wind	For Use in Open Sea	For Use on Land	Equivalent Velocity		Limits of Velocity M.P.H.
				M.P.H.	Knots	
0	Calm	Calm. Water surface smooth and glassy	Calm. Smoke rises vertically	0	0	Less than 1
1	Light air	Parts of water surface wind ruffled, with smooth patches interspersed	Direction of wind shown by smoke drift, but not by wind vanes	2	2	1 - 3
2	Slight breeze	All surfaces ruffled	Wind felt on face; leaves rustle; ordinary wind vane moved.	5	5	4 - 7
3	Gentle breeze	Small waves with occasional whitecaps	Leaves and small twigs in constant motion; wind extends light flag.	10	9	8 - 12
4	Moderate breeze	About half the wavecaps breaking	Raises dust and loose paper; small branches are moved	15	13	13 - 18
5	Fresh breeze	Entire surface broken into whitecaps	Small trees in leaf begin to sway; crested wavelets form on inland waters	21	19	19 - 24
6	Strong breeze	Tops of waves blowing off; spume	Large branches in motion; whistling heard in telegraph wires.	27	24	25 - 31
7	Moderate gale	High waves, breaking on crests.	Whole trees in motion; inconvenience felt in walking against wind	35	31	32 - 38
8	Fresh gale (Gale)	High waves, breaking on crests.	Breaks twigs off trees; generally impedes progress	42	37	39 - 46
9	Strong gale		Slight structural damage occurs (shingles blown off roof).	50	44	47 - 54
10	Whole gale		Seldom experienced inland; trees uprooted; considerable structural damage.	59	51	55 - 63
11	Storm		Very rarely experienced	68	60	64 - 75
12	Hurricane			Above 75	Above 65	Above 75

METEOROLOGICAL CODES FOR BATHYTHERMOGRAPH LOG SHEET

(Enter underlined values)

STATE OF WEATHER

Code	Description
0	Cloudless
1	Partly cloudy
2	Cloudy
3	Overcast
4	Haze
7	Distant Lightning
13	Threatening sky
14	Squally weather
16	Waterspout seen
19	Signs of tropical storm
40	Fog
49	Fog in patches
50	Drizzle
60	Rain
69	Rain and snow, mixed
70	Snow
80	Showers of rain
85	Showers of snow
88	Showers of hail, or rain and hail
90	Thunderstorm
97	Thunderstorm, heavy

STATE OF SEA

Code	Appr. Height of Sea
0	0
1	Less than 1 foot
2	1 to 3 feet
3	3 to 5 feet
4	5 to 8 feet
5	8 to 12 feet
6	12 to 20 feet
7	20 to 40 feet
8	40 feet and over
9	Confused

VISIBILITY

Code	Objects not visible at
0	50 yards
1	200 yards
2	400 yards
3	1000 yards
4	1 nautical mile
5	2 nautical miles
6	5 nautical miles
7	10 nautical miles
8	30 nautical miles
9	over 30

WIND FORCE

Beaufort	Knots	mph	Description
0	1	1	Calm
1	1-3	1-3	Light Air
2	4-6	4-7	Light Breeze
3	7-10	8-12	Gentle Breeze
4	11-16	13-18	Moderate Breeze
5	17-21	19-24	Fresh Breeze
6	22-27	25-31	Strong Breeze
7	28-33	32-38	Moderate Gale
8	34-40	39-46	Fresh Gale
9	41-47	47-54	Strong Gale
10	48-55	55-63	Whole Gale
11	56-65	64-75	Storm
12	65	75	Hurricane

METEOROLOGICAL CODES FOR BATHYTHERMOGRAPH LOG SHEET
(Enter underlined values)

TRUE WIND DIRECTION

Degrees	Direction	Compass Point
	Calm	00
000	N	32
006-016	NbyE	01
017-028	NNE	02
029-039	NEbyN	03
040-050	NE	04
051-061	NEbyE	05
062-073	ENE	06
074-084	EbyN	07
085-095	E	08
096-106	EbyS	09
107-118	ESE	10
119-129	SEbyE	11
130-140	SE	12
141-151	SEbyS	13
152-163	SSE	14
164-174	SbyE	15
175-185	S	16
186-196	SbyW	17
197-208	SSW	18
209-219	SWbyS	19
220-230	SW	20
231-241	SWbyW	21
242-253	WSW	22
254-264	WbyS	23
265-275	W	24
276-286	WbyN	25
287-298	WNW	26
299-309	NWbyW	27
310-320	NW	28
321-331	NWbyN	29
332-343	NNW	30
344-354	NbyW	31
355-005	N	32

CLOUDS

Cloud Types

Cirrus	Ci
Cirrocumulus	Cc
Cirrostratus	Cs
Nimbus	Nb
Altocumulus	Ac
Altostratus	As
Stratocumulus	Sc
Stratus	St
Nimbostratus	Ns
Cumulus	Cu
Cumulonimbus	Cb
Altocumulus castellatus .	Acc
Fractostratus	Fs
Fractocumulus	Fc
Cumulonimbus mammatus . .	Cm

AMOUNT OF CLOUDS

Enter the proportion of cloudy sky in parts from 1 to 10; thus 0 will represent "entirely clear", while 3 will represent "3/10 of the sky is obscured", and 10 represents "overcast".