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SECOND REPORT OF THE JOINT PANEL ON  
OCEANOGRAPHIC TABLES AND STANDARDS

held in

Rome, 8-9 October 1965

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United Nations Educational, Scientific and Cultural Organization

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## INTRODUCTION

1. This report follows a meeting of the panel in Rome on 8-9 October 1965. A panel meeting on 8 October was attended by:

Dr. R.A. Cox (Great Britain) in the chair  
Professor G. Dietrich (Germany)  
Dr. K.N. Fedorov (Unesco)  
Dr. N.P. Fofonoff (U.S.A.)  
Mr. F. Hermann (Denmark)  
Dr. G.N. Ivanoff-Frantzkevich (USSR)  
Professor Y. Miyake (Japan)  
Professor O. Saelen (Norway)

Guests at the meeting included Dr. Grasshoff (Germany), Mr. Menaché (France) and Dr. Morcos (Egypt). An apology for his unavoidable absence was received from Professor Carritt (U.S.A.).

On 9 October an open meeting was held, attended by a number of delegates to the annual meeting of ICES, which was in progress in Rome. In addition to the members of the panel, about 25 scientists were present. The chairman gave an account of the recent work, and of the decisions of the panel, which will be discussed later in this report. Mr. Maurice Menaché (France) read a paper entitled "Variation de la Masse Volumique de l'eau en fonction de sa Composition Isotopique." As this paper will shortly be published in "Cahiers Oceanographiques" it is not included with this report, but will be referred to in section 2c.

The chairman introduced two papers by Messrs. H. Charnock and J. Crease (Great Britain) entitled "The specification of salinity estimators" and "A salinity estimator based on conductivity ratio", (these papers are appended to this report as appendices A and B) and a short paper by Dr. J.S.M. Rusby (Great Britain) on "Measurement of refractive index of sea-water samples". (Appendix C).

The open meeting was followed on the afternoon of 9 October by a further committee meeting. It was resolved that this report should be prepared, to make known and explain the decisions of the committee. The chairman agreed to prepare a provisional draft, and Dr. Fofonoff and Professor Miyake undertook to draft certain sections. Dr. Fedorov promised that the report would be published in the series of "Unesco technical papers in Marine Science".

This introduction is followed by an account by the chairman of the work done since the last report (October 1964).

## 2. WORK COMPLETED SINCE THE LAST REPORT OF THE PANEL

### (a) Chlorinity determinations

At the last meeting of the panel (Charlottenlund, October 1964) it was resolved that in view of the importance to future work, and of the doubts which had been raised regarding the reliability of the determinations of chlorinity by Riley and his co-workers, it was necessary to repeat at least a considerable proportion of these chlorinity determinations. This has been done. In the original

measurements (see Cox, Culkin, Greenhalgh and Riley, 1962) about 450 samples were analysed. It was arranged that about 350 of these should be analysed again; the samples were divided between Dr. Riley at Liverpool University and Dr. Culkin at the National Institute of Oceanography. From this total about 100 samples were selected where a good supply of water was still available, and these were re-measured by both analysts. In addition to redetermining the chlorinity, Dr. Culkin also rechecked the conductivity ratio, in most cases using only one tube of water for both measurements.

The results are discussed in detail in the report by Charnock and Crease (Appendix B) but will be summarized here. Statistical treatment shows quite clearly that Dr. Culkin's results are very decidedly more consistent than Dr. Riley's, while there is no significant improvement in Dr. Riley's second set of determinations compared with his earlier set. Using each set of determinations on its own, a fourth order curve was fitted by least squares, expressing chlorinity as a function of conductivity ratio. The standard deviation of Dr. Culkin's chlorinities from the curve was about 0.002‰, while Dr. Riley's was over 0.006‰. The mean square difference between Dr. Riley's first and second determination on the same sample was also over 0.006‰.

The reasons for the inaccuracies in Riley's measurements are not at present clear. They are not shown in replicate determinations at one time on one sample; for such replicates the standard deviation is much less, about 0.001‰. The basic differences in the methods used are two; firstly, Culkin weighs both the sea water and the strong silver nitrate used in the titration, while Riley weighs only the water and uses a burette to measure the silver; secondly, although both workers use an electrometric end-point, the electrode systems are different. Riley's technique is described in Bather and Riley (1953), while Culkin's are based on those of Hermann (1951).

The samples determined by Dr. Culkin cover the whole range of salinity from Baltic water to Red Sea. They have not, however, been selected specifically to cover the whole range at close intervals. If these results were to be used alone to compute conductivity/chlorinity relationships, it might be necessary to undertake a few extra measurements to fill in gaps in the series, especially at low salinities.

#### (b) Conductivity/salinity tables

Based on Dr. Riley's chlorinity values, tables have been computed connecting conductivity ratio at 15° with salinity. The salinity range is 30-42‰ and the interval 0.00001 in conductivity ratio. In addition, a second table gives corrections to conductivity ratio when measured at temperatures other than 15°. These two tables had been printed in the format agreed at the previous meeting, and copies were distributed for inspection.

The chairman also distributed a copy of the computer print-out for a table covering the range 3-42‰ in salinity, at intervals of 0.0001 in ratio. He also showed a temperature correction table for this wider range, but explained he was not yet satisfied with the results from which these corrections were computed. A more extensive series of measurements was under way. (These are now finished. See section 3. Editor).

(c) Density determinations

No actual determinations had been made in the last year. The apparatus for specific gravity measurements was under reconstruction. It should be working in its improved form early in 1966.

However some work had been done on the preparation of water suitable for use as reference in specific gravity work.

Mr. Menaché's report (see section 1) shows that substantial variations exist in the isotopic ratios of natural waters, and these have a significant effect on the specific gravity. Variations in the isotopic ratios of sea water, however, are very much smaller than between, for example, sea water and polar snowfall. It would seem that water distilled from sea water should offer a suitable standard for specific gravity measurement.

The chairman circulated copies of a report (N.I.O. internal report C5. "Distilled water for relative density standard" by R.A. Cox and M.J. McCartney, March 1965) which would shortly be published in the literature. (In Deep-Sea Research - Editor.) It had been found possible to distil pure water from sea water in such a way that the isotope ratios were not significantly changed. This was confirmed by isotopic analysis of the distillate and of water similar to the original sea water.

The isotopic analyses (kindly undertaken by Professor Dansgaard in Copenhagen show that our distilled water is fractionally higher in heavy isotopes of hydrogen and oxygen than is Standard Mean Ocean Water (Craig, 1961). The results of Menaché, however, indicate that this small difference will not introduce a significant difference in density. Such distilled water seemed very suitable as a standard for specific gravity determinations.

(d) Refractive index determinations

The chairman presented a short report by Dr. Rusby (see Appendix C). The measurements at 20° were very encouraging, and could form the basis for tables connecting refractive index anomaly ( $\Delta n$ , the difference between the refractive index of the sample and that of water of salinity 35‰) and salinity or chlorinity. However there was some evidence that  $\Delta n$  depended somewhat on temperature, so that as with conductivity/salinity tables a temperature correction might be needed. Measurements were in progress at various temperatures, from which this correction could be computed.

(e) Absolute conductivity apparatus

This apparatus was complete, and working. The final trials had to await the calibration of the thermometer, precision resistors and length standards by the N.P.L. However a preliminary trial run had given a value for the conductivity of sea water of salinity 35‰ at 15° of 0.04286 ohms<sup>-1</sup> cm<sup>-1</sup>, compared with the figure of 0.04288 interpolated from the results of Thomas et al (1934).

If all went well with the calibrations, the apparatus should be tested and operational early in 1966. It would then be taken over by the Standard Sea Water Service, and used to standardize the conductivity of the standard water. The label on the standard water would then show the conductivity (and salinity computed from it) as well as the chlorinity.

### 3. THE NEW CONDUCTIVITY-CHLORINITY TABLES

The new tables for converting conductivity measurements to salinity will be distributed early in 1966, and the panel feels it appropriate to restate the reasons leading to the preparation of the tables, and the principles which have directed the work.

Because there is no general agreement, even among English-speaking scientists, on the exact meaning of some terms which will be used in this section, definitions are given below, and where these terms are used hereafter in this section it will be in accord with these definitions.

Determine, determination. A determination is an actual measurement of the variable concerned, the accuracy being limited only by the experimental limitations of the method.

Estimate, estimation. An estimation is a value for one variable derived from a determination of another; for example, we may determine chlorinity, and from the chlorinity estimate specific gravity. The accuracy of the result depends not only on the precision of the chlorinity determination, but also on our knowledge of the conversion factor, and on any natural scatter in this factor due, for example, to variations in sea water composition.

Accuracy. The difference between the result obtained and the true result, a high accuracy implying a small difference and a low accuracy a larger difference.

Precision. The difference (usually expressed as the root mean square difference, or standard deviation) between a single result and the mean of a large number of results by the same method. The precision represents the reproducibility of a method; it is not the same as the accuracy, because the method may be a bad one, and give a wrong answer. Thus a method may be precise, because it gives a consistent answer, but still be inaccurate, because the answer is wrong.

We all know the general concept of salinity. It expresses the concentration of dissolved solids in sea water, measured in parts per thousand of sea water by weight. Unfortunately, salinity is a very difficult quantity to determine directly, and it has been necessary in practice to estimate salinity from measurements of some other parameter. The problem facing the panel is to ensure that whatever method is used for salinity estimation, the final figure which we obtain will be as nearly as is possible the same.

During the discussion in Rome, Dr. Fedorov put forward a very helpful analogy between salinity and temperature. Like salinity, temperature is a concept rather than a clearly defined property. It expresses the heat-content of matter, just as salinity expresses salt content of water. We cannot measure temperature directly; what we measure is some property dependent on it, such as the expansion of mercury

or the resistance of a platinum wire. Both concepts have their absolute zero-with temperature, when all thermal energy is absent; with salinity, when the water is pure and free of salt. Unfortunately with salinity we do not have any other fixed points, like the freezing and boiling points of water which assist in fixing temperature scales.

The traditional parameter used for estimating salinity is the chlorinity determination, which measures chloride and bromide in the sea water by weight, usually by a volumetric procedure using a standard sea water as reference. The chlorinity scale was defined by Jacobsen and Knudsen (1940) with pure silver as the standard. The only assumption in this definition is that the ratio of chloride to bromide in sea water is constant; the available evidence, including that from the recent work, shows that this assumption is justified as nearly as we can tell.

Salinity has usually been estimated from chlorinity by the equation proposed by Forch, Knudsen and Sørensen (1902), which is based on determinations of chlorinity and salinity on a number of natural sea waters, including several from the Baltic Sea. From these analyses the well known relationship

$$S \text{ ‰} = 1.805 \text{ Cl ‰} + 0.03$$

was deduced. To obtain this equation, Sørensen defined "salinity" in an arbitrary way, which is certainly related to the dissolved salts, but disregards the bicarbonate and some other volatile ions. The constant 0.03 represents approximately the solid content of river water flowing into the Baltic, disregarding the bicarbonate ion. This solid content is partly calcium sulphate, but mostly calcium bicarbonate which in the Sørensen salinity determination is converted to oxide, and weighed as such. Conductivity measurements, however, estimate also the bicarbonate ions, as well as traces of other volatile components such as organic acids which are not measured in the Sørensen methods. Thus if we prepare an equation between salinity and conductivity ratio, (R), defining salinity as chlorinity multiplied by a constant, we get

$$S \text{ ‰} = x \text{ Cl ‰} = aR + bR^2 + cR^3 + \text{----} -0.09$$

The intercept, 0.09 ‰, is the apparent salinity at zero chlorinity, and represents dissolved ionic material in river water, whereas the Sørensen 0.03 ‰ represents (mainly) calcium oxide. Thus if we wish to prepare an expression relating conductivity and salinity, to include Baltic Sea samples, and to make our "salinity" the best possible measure of ionic content, then we should start by estimating salinity from our chlorinities using

$$S \text{ ‰} = 1.802 \text{ Cl ‰} + 0.09$$

rather than the Sørensen formula.

The real point is this; even when dealing with samples from the Baltic Sea, the Sørensen 0.03 has a real significance only when referred to an arbitrary method of determination, and has little meaning when considering conductivity measurements. This is even more true when considering other low salinity waters, as there is no evidence that the conductivity at zero chlorinity would correspond with that found in the Baltic area.



A further problem arises when considering dilution of sea water by pure water. When sea water is diluted by rain, or by melting polar ice, it is convenient to calculate the salinity of the diluted water from the weights of salt water and fresh water in the mixture. If we define salinity as a  $Cl\% + b$ , then the salinity of the mixture is not in direct proportion to that of the constituents; for example, if a given weight of salt water is diluted with an equal weight of fresh, the chlorinity in the mixture will be half the original value, but the salinity will not. This is confusing, and in a relationship claiming to be a weight ratio, grammes per kilogramme of water, it is quite illogical.

The simple solution to all these problems would seem to be to abandon the term salinity, and report our observations as conductivity ratio or chlorinity. The second alternative, to report as chlorinity, has the objection that conductivity and chlorinity are not exactly related, due to variations in composition of sea water. Some means must be used to distinguish actual chemical chlorinity determinations, (which are often valuable data) from conductivity measurements. Conductivity, however, has at present little significance to most oceanographers, and none at all to many, particularly those such as biologists and geologists not directly concerned with salinity measurements. To most people reading this report a salinity of 33.04 ‰ will mean something; a conductivity ratio of 0.950 will not. Also the various data centres are equipped to record salinity, not conductivity; millions of such records exist, and it would be prohibitively expensive to change them.

There is no simple solution to all these problems. Whatever procedure is adopted by the panel, some embarrassment will be caused to some oceanographers. The panel has given long consideration to the alternatives, and to the comments and criticisms put forward after publication of the first report. The recommendations of the panel are these.

- (1) That in future, chlorinity determinations should preferably be reported as such, and not converted to salinity estimates.
- (2) That when it is necessary to estimate salinity from chlorinity determinations, the equation  $S\% = 1.80655 Cl\%$  should be used rather than the Sørensen equation.
- (3) Salinity shall be redefined as a function of conductivity ratio.
- (4) An equation shall be computed from Dr. Culkin's measurements of chlorinity and conductivity ratio on the natural sea water samples held by the N.I.O. Samples from the Baltic and Black seas, and other low salinity areas, shall be included, and only samples collected near the surface shall be used. For the purpose of computing the equation, salinity shall be estimated from the original chlorinity determinations by the equation  $S\% = 1.80655 Cl\%$ . Using the salinity estimates so obtained, and the corresponding conductivity ratios, an equation shall be computed by the method of least squares giving salinity as a function of conductivity ratio (R).
- (5) This equation shall constitute the definition of salinity.
- (6) The new tables connecting salinity and conductivity ratio shall be derived from this equation.

The procedure proposed will have these advantages. The salinity so defined can readily be determined by the conductivity method, which is the most precise method at present available. It is intended that Standard Sea Water shall be used as a conductivity standard, and will be certified as such (see section 5). Salinity so defined is conservative, and can be calculated by simple proportion either when mixing different sea waters, or when mixing sea water with fresh water. In the ocean range (salinity 32-39 ‰) the new salinity will agree within the normal precision of determination with earlier estimates based on chlorinity determination and the the Sørensen equation. The actual difference is zero at 35 ‰, and 0.0023 ‰ at 32 ‰ and 38 ‰.

The only area where these decisions may cause some problems is the Baltic Sea. Here salinity determined from conductivity measurements and the new tables will differ from earlier estimates, based on chlorinity, by about 0.02 ‰ at 11 ‰ and 0.025 ‰ at 6 ‰. This discrepancy is about the same as the precision of normal chlorinity determinations, and in view of the wide variations of salinity which prevail in the Baltic, the panel do not consider that such a change will cause much difficulty. We hope that the Baltic oceanographers will agree with our recommendations, as it is clearly desirable that the same nomenclature and definitions shall be used in all parts of the world.

Based on these decisions, the new tables have been prepared, and at the time of writing (February 1966) are ready for printing. The tables are based on determinations of chlorinity and conductivity ratio at 15°C ( $R_{15}$ ) made on 135 samples of natural sea water, including samples from all oceans and from the Baltic, Black, Red and Mediterranean Seas. Salinity was estimated from chlorinity using

$$S \text{ ‰} = 1.80655 C_1 \text{ ‰}$$

and a fifth order polynomial computed by least squares giving salinity as a function of  $R_{15}$ , with a small correction to the constant term (+ 0.00018 ‰) to make  $R_{15} = 1.0$  correspond with  $S = 35 \text{ ‰}$ .

$$S \text{ ‰} = -0.08996 + 28.2972R_{15} + 12.80832R_{15}^2 - 10.67869R_{15}^3 + 5.98624R_{15}^4 - 1.32311R_{15}^5$$

This equation constitutes the recommended definition of salinity.

Table Ia, based on the above equation, connects  $R_{15}$  with salinity, and is designed for use with thermostat salinity meters working at 15°. A second table (table Ib) gives corrections to conductivity ratio measured at any temperature between 10° and 30°, to give the equivalent value of  $R_{15}$ . This table is based on measurements of conductivity ratio at various temperatures with an Auto-Lab wide-range inductive salinometer. The correction ( $\Delta_{15}$ ) to bring conductivity ratio at temperature  $T^\circ$  ( $R_t$ ) to the ratio at 15° ( $R_{15}$ ) is given by

$$\Delta_{15}(T) = R_{15} - R_t = 10^{-5} R_t (R_t - 1) (T - 15) [96.7 - 72.0R_t + 37.5R_t^2 - (0.63 + 0.21R_t^2)(T - 15)]$$

The values of  $\Delta$  computed from this expression are considered to be accurate to within  $\pm 0.05 \Delta$  for temperatures between 10° and 30°.

For the greater convenience of those using non-thermostat salinometers, a second set of tables (tables IIa and IIb) have been computed from the same data as tables Ia and Ib, but based on conductivity ratio at 20° ( $R_{20}$ ) and covering the range of  $R_{20}$  from 0.1 to 1.2 (salinity about 3 to 42 ‰). These tables give

exactly the same values of salinity as Ia and Ib, but since most measurements on non-thermostat meters will be made at temperatures close to 20°, it will often be legitimate to neglect the small corrections given by table IIb, especially when salinities are near 35 ‰.

The tables will have brief introductions, indicating how they shall be used, and in accord with standard Unesco practice these will be in English, French, Russian and Spanish. The tables will be printed on separate sheets and bound in a loose-leaf binder with stiff covers, lettered "International Oceanographic Tables" in the four languages. The binder will be large enough to accommodate additional tables as they are available.

The panel think it necessary to point out that these new tables (on loose sheets, in stiff-cover binder) are not quite identical with the provisional tables referred to in section 2 (b). (bound in buff-coloured paper cover). A few copies of the provisional tables have been distributed for special purposes. As soon as the new tables are available, please destroy any copies you may have of the provisional tables. Sample sheets of the new tables are appended to this report (Appendix D).

#### 4. FURTHER TABLES TO BE ISSUED

Further tables already under consideration for the series include:

- (a) effect of pressure on conductivity of sea water;
- (b) specific gravity from temperature and salinity;
- (c) chlorosity from chlorinity or salinity;
- (d) velocity of sound, from temperature, pressure, salinity;
- (e) salinity from refractive index.

The panel will welcome suggestions for additions or improvements to the tables. These may be sent to any member of JPOTS.

There was a discussion on the best form for specific gravity ( $\sigma_t$ ) tables. The last panel report included samples of existing tables, and asked for recommendations. None had been received. After some debate, it was agreed that nomograms were to be preferred to tables, because more information could be conveyed on a page. Two nomograms are enclosed with this report (Appendix E) illustrating one possible format. Comments on this arrangement, and on possible alternatives, will be welcomed.

#### 5. STANDARD SEA WATER AS A CONDUCTIVITY STANDARD

None of the conductivity salinometers at present in use measures conductivity directly, in reciprocal ohms per cm. All are designed to measure either as a ratio to a standard water, or are calibrated so as to read in salinity or chlorinity. Without exception they all need a sea water of known salinity for calibration purposes.

It has been customary for some years to use Copenhagen Standard Water as such a standard. To guard against any unforeseen variation in composition, for the last three years each new batch of standard water has been checked for relative conductivity at the N.I.O., using at least two earlier batches as standard in each case. No really significant variations have occurred during this time, that is the conductivity ratio has corresponded with the chlorinity within the normal precision of salinometers.

This procedure is not entirely satisfactory. It would be embarrassing if a batch of standard water was found to have a conductivity which did not correspond with the chlorinity. Also there is some evidence that conductivity of standard water may apparently increase slightly on prolonged storage, especially at elevated temperatures (see Park, 1964).

To overcome this problem the N.I.O. (as mentioned in section 2 (e)) have designed and built an apparatus for the direct measurement of the conductivity of each batch of standard water. This apparatus will also be used for a research programme to study the change in conductivity consequent on storage under different conditions, such as high temperature or mechanical oscillation as on board ship.

The apparatus measures the resistance of standard water contained in a fused silica cell of known dimensions, comparing this with a standard non-inductive resistor on a transformer bridge. The cell is held in a thermostat at 15°C. This temperature must be known to  $\pm 0.001^\circ\text{C}$ , which presents a difficult problem. The apparatus originally ordered for this function has proved unreliable, and a new quartz-crystal thermometer has been ordered. Unfortunately there is a delay in the delivery of this thermometer, but as soon as it is available the proving trials of the conductivity meter will be started.

It is hoped to have all new batches of standard water certified in conductivity (salinity) from about June of 1966. Used in combination with the new tables, which should be distributed before this time, all oceanographers will have a reliable and uniform basis for their salinity measurements.

#### REFERENCES

- Bather, J.M., & J.P. Riley (1953) J. Cons. int. Explo. Mer, 18, 277  
Cox, R.A., F. Culkin, R. Greenhalgh & J.P. Riley (1962) Nature, 195, 518  
Craig, H. (1961) Science 133, 1835  
Forch, C., M. Knudsen & S.P.L. Sørensen (1902) Kgl. Danske Videnskab. Selskabs Skrifter, 7 Række, Naturvidensk. og Mathem. Afd. 12, 1  
Hermann, F., (1951) J. Cons. int. Expl. Mer, 17, 223  
Jacobsen, J.P. & M. Knudsen (1940) U.G.G.I. Assoc. Oceanogr. Phys. Publ. Sci. 7, 1  
Park, K. (1964) Deep Sea Res. 11, 85  
Thomas, B.D., T.G. Thompson & C.L. Utterback (1934) J. Cons. int. Expl. Mer, 9, 28

## THE SPECIFICATION OF SALINITY ESTIMATORS

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INTRODUCTION

Some of our colleagues are engaged in making precise measurements of the properties of sea water. They consult us, from time to time, about the statistical aspects of their observations and we have been asked for our views on the present status of the observations of chlorinity and conductivity ratio.

We have found it impossible to discuss this and allied problems usefully unless the words and symbols used are explicitly defined. The definitions we have found most satisfactory will be given and described in the hope that they will be considered by the joint ICES/IAPO/SCOR/Unesco Committee dealing with the problem.

TERMINOLOGY

The main need we have found is for the term "salinity estimator" to describe the relations now in use, or proposed, from which the "salinity" can be estimated from an observation of another variable, such as chlorinity or conductivity ratio.

In what follows a symbol without suffix (e.g. Cl) will represent a measured quantity (in this case chlorinity).

An estimator will be a precise mathematical function of a measured quantity and will be written as a symbol with a suffix. For instance, we shall write  $Cl_3 = f_3(R)$  meaning that the estimator  $Cl_3$  is exactly defined as a known function of the conductivity ratio  $R$ .

The word regression we shall use to describe a relationship between two variables which are highly correlated but not exactly related. Thus for example,

$$Cl = f_3(R) + \epsilon_3$$

is a regression. It means that in a particular set of observations of  $Cl$  and  $R$ , the values of  $Cl$  were statistically related (for example, in a least squares sense) by the function  $f_3(R)$ , the residual on a particular single observation being  $\epsilon_3$ . The residuals  $\epsilon_3$  will be in part experimental errors and in part due to small changes in the proportions of the major constituents of sea water.  $Cl_3 = f_3(R)$  will be an estimator derived from the regression by dropping the residuals  $\epsilon_3$ .

THE DEFINITION OF SALINITY

At the second International Conference of ICES at Kristiania, 1901, it was resolved: that by salinity is to be understood the total weight in grammes of solid matter dissolved in 1,000 grammes of (sea) water.

According to Cox (1965) this definition in terms of total solids has not been revoked or superseded. However, there is throughout the literature the more usual definition, based on Sørensen's work; the salinity is the total amount of solid material in grammes contained in one kilogram of sea water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine and all organic material completely oxidized.

Neither the total solids nor the "Sørensen-salinity" can be measured with precision so that both definitions are in the nature of a concept. This is clearly preferable to any definition based solely on an experimental procedure, which could be altered by future developments in analytical technique.

We may note that, although salinity has not been defined in a form which would permit precision determination, no serious practical difficulty has arisen in its interpretation. Oceanographers have come to regard the salinity as related in an approximate way to the salt concentration and are accustomed to estimating it from measurements of other properties. It is with the definition of these salinity estimators that we are mainly concerned.

#### SALINITY ESTIMATORS

The measured variables which we shall use are:

- (a) The Sørensen-salinity (S) is the result obtained by following Sørensen technique for estimating the salinity as commonly defined.
- (b) The Chlorinity (Cl) is as usually defined, bearing an analogous relation to the chloride content as the Sørensen salinity bears to the dissolved solids. The silver nitrate used in the chlorinity determination is usually standardized relative to standard sea water whose chlorinity, in turn, is determined with reference to pure silver by the standard sea water service, Copenhagen.
- (c) The conductivity ratio (R) we define as the ratio of the electrical conductivity of a sample of sea water relative to that of a standard value of electrical conductivity, at a standard temperature. Until a suitable standard is available measurements have been made against a particular batch of standard sea water at a temperature of 15°C.

The salinity estimators (and the chlorinity estimators) based on measurements of these variables are now considered. Figure 1 is an attempt to illustrate the procedures.

- (1) S and Cl are defined quantities: apart from experimental error they estimate "salinity" and "chlorinity" respectively. One can write formally

$$S_1 = S \quad \text{and} \quad Cl_1 = Cl$$

to separate the estimate from the observation.

- (2) S<sub>2</sub> is a salinity estimator based on observations of S and Cl. Only one series of nine measurements is known (Sørensen 1901) and these provide the regression

$$S = f_2(Cl) + \epsilon_2 = 1.805 Cl + 0.03 + \epsilon_2$$

where  $\epsilon_2$  is a residual, in part experimental, of order 0.01 ‰.

The estimator is then defined as

$$S_2 \equiv f_2(C_1) \equiv 1.805 C_1 + 0.03$$

by dropping the residual  $\epsilon_2$ .

It is important to distinguish between salinity estimators such as  $S_1$  and  $S_2$ .  $S_2$  is determined exactly by  $C_1$  but  $S_1$  is not. Differences will arise to the extent that the major constituents of sea water occur in different proportions.

(2A) Some workers have preferred to express the  $S/C_1$  regression as

$$S = f_{2A}(C_1) + \epsilon_{2A} = 1.80655 C_1 + \epsilon_{2A}$$

so as to maintain consistency with the hypothesis of constant composition. This would not conflict with the original  $S$  determinations. It leads to a salinity estimator.

$$S_{2A} \equiv f_{2A}(C_1) \equiv 1.80655 C_1$$

Salinity estimates based on chlorinity titration ( $S_2$ ) were for many years referred to as "salinities" without qualification. Since the titration was the most convenient method, and since the differences between  $S_1$  and  $S_2$  were in general smaller than the experimental error, no serious confusion arose.

The development of "salinometers" based on measurements of conductivity ratio created the need for a salinity estimator based on conductivity ratio.

(3) We seek a salinity estimator based on conductivity ratio

$$S_3 \equiv f_3(R)$$

The steps we propose are as follows (see Figure 1).

From a series of careful measurements of  $C_1$  and  $R$  one writes a regression

$$C_1 = f_3(R) + \epsilon_3$$

leading to a chlorinity estimator

$$C_{12} = f_3(R)$$

This is then substituted into  $f_{2A}(C_1)$  to get

$$S_3 \equiv f_{2A}(C_{12}) \equiv f_{2A}(f_3(R))$$

This will define a salinity estimator based on conductivity ratio which is consistent, within residual error, with  $S_1$  and  $S_{2A}$ .

As a result of recent work observations are available from which the  $C_1/R$  regression can be specified. The present position of these observations will be discussed later.

Further estimators  $S_4$ ,  $S_5$  etc. can be defined as needed. An estimator  $S_4$  based on observations of chlorinity and density ratio is indicated on Figure 1. New estimators might also be based on the results of further series of observations of, say,  $S$  and  $C_1$ . We have limited the notation  $S_2$ ,  $S_{2A}$  ( $S_{2B}$ ) etc. to differing ways of expressing the same set of observations.

CONCLUSIONS

The procedure outlined defines the various salinity estimators and ensures consistency between them so far as is possible. Any one of them will be adequate for work where the highest accuracy is not needed.

However we must again state that the estimates  $S^1$ ,  $S^2$ ,  $S^3$  etc. based on error-free observations on the same sea water may differ. Any differences which are established will pose an important oceanographic problem. It is therefore important that they shall be clearly defined.



<u>Basic Property</u>	<u>Dissolved Solids</u>	<u>Chlorinity</u>	<u>Conductivity</u>	<u>Density</u>
Estimators Salinity Chlorinity	$S_1 = S$	$S_2 = f_2(Cl)$ $S_{2a} = f_{2a}(Cl)$ $Cl_1 = Cl$	$S_3 = f_{2a}(Cl_2) = f_{2a}(f_3(R))$ $Cl_2 = f_3(R)$	$S_4 = f_{2a}(Cl_3) = f_{2a}(f_4(\sigma))$ $Cl_3 = f_4(\sigma)$
Regressions		$S = f_2(Cl) + \xi_2$ $S = f_{2a}(Cl) + \xi_{2a}$	$Cl = f_3(R) + \xi_3$	$Cl = f_4(\sigma) + \xi_4$
Measured Quantities	Sørensen salinity (S)	Chlorinity (Cl)	Conductivity Ratio (R)	Density Ratio ( $\sigma$ )

- NOTES**
- None of the basic properties has been satisfactorily measured.
  - Variables without suffixes are observed quantities.
  - Variables with suffix are estimated quantities.
  - $\xi$  represents the deviation of a single determination from a mean curve.
  - $S_1$  and  $Cl_1$  are the currently accepted definitions of salinity and chlorinity.

Figure 1 - Derivation of salinity estimators

A SALINITY ESTIMATOR BASED ON MEASUREMENTS  
OF CONDUCTIVITY RATIO

by

H. Charnock and J. Crease

INTRODUCTION

This note gives a preliminary assessment of the material now available for the definition of a salinity estimator based on measurements of the conductivity ratio. It is written at the request of Dr. R.A. Cox and for the guidance of the Joint ICES/IAPO/SCOR/Unesco committee concerned with this subject. It should be read in conjunction with an accompanying paper on the specification of salinity estimators.

OBSERVATIONAL MATERIAL

1. Conductivity ratio

Observation on which the salinity estimator ( $S_3$  in an earlier paper) may be based have been made on samples of sea water widely distributed over the ocean and from various depths.

The conductivity ratio ( $R$ ) for each sample was determined by Dr. F. Culkin, National Institute of Oceanography, relative to standard sea water batch P31, at 15°C. The chlorinity of this batch is 19.375‰, and the corresponding value of salinity estimate  $S_2 = 35.002$ . A small correction was made to the primary measurements to get the conductivity ratio relative to standard sea water of  $S_2 = 35.000$ . This correction was based on earlier approximate measurements and will be consistent with the salinity estimator  $S_3$  finally specified.

Repeat determination of conductivity ratio agreed within about 0.00005 provided the samples were drawn from sealed ampoules. No effect of storage was found.

Values measured on water from fully opened ampoules, from which chlorinity samples had been drawn, were greater by a few parts in  $10^5$  than those made earlier. As other workers have found an increase in  $R$  on opened samples we have not used these values further.

2. Chlorinities

All the chlorinities ( $C_1$ ) were determined at the Department of Oceanography, University of Liverpool, in the first instance. These observations will be referred to as Liverpool I. Chlorinities for some of the samples have been re-determined at Liverpool (Liverpool II) and at the National Institute of Oceanography (N.I.O.). A small number of chlorinities were also measured at the Standard Sea Water Service, (Copenhagen).

Apart from this latter set, which will be discussed later, three overlapping sets of observations have been directly compared:

- |  |             |
|--|-------------|
| 1. Liverpool I and Liverpool II and N.I.O. | 102 samples |
| 2. Liverpool I and Liverpool II            | 155 samples |
| 3. Liverpool I and N.I.O.                  | 173 samples |

In each case the chlorinity was expressed as:

$$C_1 = a_0 + a_1(R) + a_2(R^2) + a_3(R^3) + a_4(R^4) + \epsilon$$

where R is the conductivity ratio of the same water. The constants  $a_0$  .....  $a_4$  were chosen by a least square method (preliminary working having shown that curves of higher order than four did not reduce the r.m.s. deviation significantly). It is clear that the N.I.O. deviations are smaller than those of the Liverpool observations by a factor greater than 3. The standard deviation of the N.I.O. observation about the fitted curves is about 0.002‰. The standard deviation of the differences between Liverpool I and Liverpool II is about 0.006‰.

This indicates that the casual errors of the N.I.O. observations are significantly less than those of Liverpool I or Liverpool II or of their combination. Possible systematic differences are more difficult to assess but some indication can be obtained from the results of eight comparative measurements of chlorinity made at N.I.O. and at Copenhagen.

The N.I.O. observations are systematically less than those done at Copenhagen by only  $0.0015 \pm 0.0008$  ‰. Though this latter difference is small it is statistically significant at the 1% level; the experimental error of N.I.O. replicates is about 0.001‰, and the corresponding figure for Copenhagen about 0.005‰.

The possibility that this systematic difference arises from the use of different batches of standard sea water is being investigated.

But it is clear that the N.I.O. determinations of chlorinity and conductivity ratio provide the best material currently available to us for the definition of salinity estimator  $S_3$ , which in turn is based on  $C_1$ .

#### THE $C_1/R$ REGRESSION

Two possible definitions of  $C_1$  are being considered, one using all the N.I.O. observations, the other using only those N.I.O. determinations made on surface samples.

It is desirable, though not essential, that  $S_3 = 35.000$  when  $CR = 1.00000$ . This could most easily be achieved by adding a suitable constant ( $\mp 0.0005$ ) to the  $C_1$  values. This arbitrary adjustment can be partly justified by the results of the N.I.O./Copenhagen comparisons: it is not likely to be significant in routine work.

If there are significant differences between estimators based on surface and on all samples, we recommend that  $S_3$  and  $C_1$  should be defined by the regression, to sufficiently high order, of  $C_1$  on  $CR$ , the values being those determined at N.I.O. on surface samples, each  $C_1$  value being increased by a constant amount to ensure that  $C_1 = 19.3740$  when  $CR = 1.00000$ .

Preliminary analysis shows that tables produced on this basis will differ from those which have already been constructed using a combination of N.I.O. conductivity ratios and Liverpool chlorinities (Unesco, undated). Although these differences are unlikely to exceed 0.005% in Cl<sub>2</sub> this is considerably greater than the standard error of a single N.I.O. or Copenhagen determination. It would be prudent in our opinion to withdraw these Unesco tables before they are widely circulated.

The earlier results suggested that S<sub>4</sub> (the salinity estimate based on observation of density ratio) is more closely related to S<sub>3</sub> (based on conductivity ratio) than to S<sub>2</sub> (based on chlorinity). The specification of S<sub>4</sub>, in terms of density ratios and chlorinities determined at N.I.O., is now under consideration. In the meantime the earlier conclusion should be regarded as tentative until it is confirmed.

### CONCLUSIONS

We recommend that the Committee issue, with a full account of their construction, tables by which salinity can be estimated from measurements of conductivity ratio.

These should, in our opinion, be based on measurements of chlorinity and conductivity ratio made at N.I.O.

Tables based on other measurements should be withdrawn and conclusions based upon them treated with reserve.

REPORT ON THE MEASUREMENT OF REFRACTIVE  
INDEX OF SEA WATER SAMPLES

by

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National Institute of Oceanography

A Jamin interferometer has been used in a temperature controlled room to measure the difference in refractive index between test samples and Copenhagen sea water. It is possible to read fringe displacement to better than 1/30th fringe which would give a theoretical accuracy of 2 in the 7th decimal place for refractive index when using the 10 cm interferometer cell. This is equivalent to a change in salinity of 0.001‰. However the practical accuracy of the measurements is limited by the temperature stability of the optical parts of the apparatus, and also the errors introduced in handling the sea water and rinsing the cell.

To date measurements of the refractive index have been made at 20°C on 40 surface water samples with salinity values evenly spaced between 30 and 39‰. These samples were specially selected for their good agreement between the measured values of chlorinity and conductivity ratio in terms of salinity units. In order to identify the integral number of fringes involved it has been found necessary to plot a curve of the gradient of the chlorinity/refractive index curve versus chlorinity. Likewise the curve of the gradient of conductivity ratio/refractive index has also been plotted. Both these curves are linear over a large part of their length which indicate that the curves of chlorinity versus refractive index and conductivity ratio versus refractive index are exponential. In salinity units the gradients decrease from

$$\frac{\partial \mu}{\partial \text{Sal}} = 0.0001885 \text{ at } 30\text{‰}$$

$$\frac{\partial \mu}{\partial \text{Sal}} = 0.0001870 \text{ at } 40\text{‰}$$

Some preliminary calculations show that the standard deviation of the measured points from the best curve in a chlorinity versus refractive index plot is 0.005‰ (salinity units).

15°

$R_{15} \rightarrow S_{\infty}$

	0	1	2	3	4	5	6	7	8
0.97 00	33. 827	827	828	828	828	829	829	830	8
01	831	831	832	832	832	833	833	834	8
02	835	835	835	836	836	837	837	837	8
03	839	839	839	840	840	841	841	841	842
04	842	843	843	844	844	844	845	845	846
05	846	847	847	848	848	848	849	849	850
06	850	851	851	851	852	852	853	853	853
07	854	855	855	855	856	856	857	857	857
08	858	858	859	859	860	860	860	861	861
09	862	862	863	863	864	864	864	865	865
0.97 10	866	866	867	867	867	868	868	869	869
11	870	870	871	871	871	872	872	873	873
12	874	874	874	875	875	876	876	876	877
13	878	878	878	879	879	880	880	880	881
14	882	882	882	883	883	883	884	884	885
15	885	886	886	887	887	887	888	888	888
16	889	890	890	890	891	891	892	892	892
17	893	894	894	894	895	895	896	896	896
18	897	897	898	898	899	899	900	900	900
19	901	901	902	902	902	902	904	904	904
0.97 20	905	905	906	906	906	907	907	908	908
21	909	909	910	910	910	911	911	912	912
22	913	913	913	914	914	915	915	915	916
23	917	917	917	918	918	919	919	919	920
24	921	921	921	922	922	923	923	923	924
25	924	924	924	925	925	926	927	927	928
26	928	928	928	929	929	930	931	931	931
27	931	931	931	932	932	933	934	934	935
28	937	937	937	938	938	938	938	939	939
29	942	942	942	942	942	942	942	943	943
0.97 30	944	944	945	945	945	946	946	947	947
31	948	948	949	949	949	950	950	951	951
32	952	952	953	953	953	954	954	954	955
33	956	956	956	957	957	958	958	958	959
34	960	960	960	961	961	961	962	962	963
35	963	964	964	965	965	965	966	966	967
36	967	968	968	969	969	969	970	970	970
37	971	972	972	972	973	973	974	974	974
38	975	976	976	976	977	977	977	978	978
39	979	979	980	980	981	981	981	982	982
0.97 40	983	983	984	984	985	985	985	986	986
41	987	987	988	988	988	989	989	990	990
42	991	991	992	992	992	993	993	993	994
43	995	995	995	996	996	997	997	997	998
44	999	999	999	000	000	001	001	001	002
45	34. 002	003	003	004	004	004	005	005	006
46	006	007	007	008	008	008	009	009	009
47	010	011	011	011	012	012	013	013	013
48	014	015	015	015	016	016	017	017	018

SAMPLE SHEET - APPENDIX "D"  
 The size of the type will be slightly reduced  
 to correspond with the standard page size.

Table Ib

Tabla Ib

Таблица Ib

$R_t$	$R_t + t^\circ \longrightarrow \Delta_{15}$							$\Delta_{15} + R_t = R_{15}$
	$20^\circ$	$21^\circ$	$22^\circ$	$23^\circ$	$24^\circ$	$25^\circ$	$26^\circ$	
0.85	-37	-44	-51	-57	-64	-70	-76	
0.86	-35	-42	-48	-54	-60	-66	-71	
0.87	-33	-39	-45	-51	-56	-62	-67	
0.88	-31	-36	-42	-47	-52	-57	-62	
0.89	-28	-34	-39	-44	-48	-53	-58	
0.90	-26	-31	-36	-40	-44	-49	-53	
0.91	-24	-28	-32	-36	-40	-44	-48	
0.92	-21	-25	-29	-33	-36		-43	
0.93	-19	-22	-26	-29	-32		-38	
0.94	-16	-19	-22	-25	-		-33	
0.95	-14	-16	-19	-21			-28	
0.96	-11	-13	-15	-			-22	
0.97	-8	-10	-11				-17	
0.98	-6	-7	-			-6	-11	
0.99	-3	-3				-11	-6	
1.00	0				0	0	0	
1.01	3			4	5	5	6	
1.02	6			9	10	11	12	
1.03				14	15	17	18	
1.04			16	18	20	22	24	
1.05			21	23	26	28	30	
1.06		22	25	28	31	34	37	
1.07		26	30	33	37	40	43	
1.08	25	30	34	38	42	46	50	
1.09	29	34	39	44	48	53	57	
1.10	32	38	43	49	54	59	64	
1.11	36	42	48	54	60	66	71	
1.12	39	46	53	60	66	72	78	
1.13	43	51	58	66	73	79	86	
1.14	47	55	63	71	79	86	93	
1.15	51	60	69	77	85	93	101	
1.16	55	64	74	83	92	101	109	
1.17	59	69	79	89	99	108	117	
1.18	63	74	85	96	106	116	125	
1.19	67	79	91	102	113	123	133	

Sample Sheet - Appendix "D"





