The Practical Salinity Scale 1978 and Its Antecedents

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Abstract—The history of the definition of salinity and the methods of computing it are traced from the beginning of the twentieth century until the present. Difficulties that have arisen in existing practices are discussed, in particular, the situation regarding reduction of in-situ CTD observations. The Practical Salinity Scale 1978 is an attempt to remove the shortcomings; it has been recommended for international acceptance. The basis for this new scale is an equation relating the ratio of the electrical conductivity of the seawater sample to that of a standard potassium chloride solution (KCl) at 15°C atmospheric pressure. The samples used were prepared from standard seawater diluted with distilled water or evaporated by weight. Finally, the set of new equations for CTD data reduction is given, based upon the work of authors whose papers are appearing elsewhere in this volume.

INTRODUCTION

As originally conceived, salinity was to provide a measure of the mass of salt per unit mass of seawater. Nearly all the problems that have arisen in applying the concept are due to an inability to determine this salinity (hereinafter termed absolute salinity $S_a$) from a single measurement. A fully detailed chemical analysis is still the only practical method and is far too time consuming for routine use. The most comprehensive early study of the composition of seawater was that made by Dittmar [1] on samples collected during the Challenger Expedition. He made 77 complete analyses of seawater, taken from various depths in the world’s oceans, excluding polar regions. The data set has frequently been taken to “prove” the constancy of ionic ratios in seawater. Cox [2] has pointed out that this is a misinterpretation of Dittmar’s statements, who, for example, found an increase in calcium content with depth but was unable to determine any regular relationship between variations and geographical position.

In 1889 the International Council for the Exploration of the Sea named Knudsen as chairman of a commission to study the problems of determining the salinity and density of seawater. Attempts were made to measure salt content by heating to remove the water from the sample by evaporation. Simple drying was accompanied by losses of volatile compounds and the hygroscopic nature of the thick residue made the measurement of its weight very difficult. A dry residue method was offered as a solution; the seawater sample was evaporated and dried to a stable weight at 480°C after processing with hydrochloric acid. On this basis, Forch, Knudsen, and Sørensen [3] defined salinity as “the total amount of solid material in grams contained in one kilogram of seawater when all the carbonate has been converted to oxide, all the bromine and iodine replaced by chlorine, and all the organic material oxidized.” Even this process had great technical difficulties and was extremely difficult to carry out aboard a ship. Based on the premise of the constancy of ionic ratios in seawater, the commission defined a “chlorinity” that could be determined by a simple volumetric titration using silver nitrate, to be used as a measure of salinity. Chlorinity was defined as “the weight in grams (in vacuo) of the chlorides contained in one gram of seawater (likewise measured in vacuo) when all the bromides and iodides have been replaced by chlorides.” Knudsen and his colleagues made measurements on samples of seawater from the surface of the Baltic, Mediterranean, and Red Seas, as well as from the North Atlantic Ocean and on the basis of comparison of nine determinations of salinity and chlorinity as defined above, proposed the formula

$$S_a^\circ = 0.03 + 1.805 Cl^\circ$$

(1)

which served oceanographers for the next 65 years. The conversion of the results of the titration into chlorinity required a knowledge of atomic weights and it was realized that these might alter as the accuracy of scientific measurement improved. Thus it was specified that the results of the chlorinity titration should be reduced using the tables produced by the commission based upon Copenhagen Normal Water as the standard. In practice this means that the chlorinity of (1) is defined in terms of 1902 atomic weights as at that time the normal water itself was related to an original potassium chloride (KCl) standard. In order to free chlorinity values from dependance on the store of normal water at Copenhagen, Jacobsen and Knudsen [4] established a new description for chlorinity as the mass of silver required to precipitate completely the halogens in O.3285234 kg of sample seawater. This is the current definition.

From their definitions both chlorinity and salinity should be conservative properties, that is, that dilution of a given sample by an equal mass of pure water should halve both those variables. Yet (1) does not allow both variables to be conservative simultaneously and makes their definitions inconsistent. At 0.00%_o chlorinity one is left with 0.03%_o of salt content by weight which must reflect the inadequacy of the titration to represent a mass-type measurement in low salinity water.

The lower salinity samples used by Knudsen to derive (1) came from the Baltic, where runoff from the land is a dominant influence in determining the ratio of the ions in solution. Equation (1) reflects the inadequacy of one ion, chlorine, to represent the total ionic content under these conditions. In later years it was found that Knudsen’s equation...
is a particular example of general equation

\[ S = A + B \text{Cl.} \]  \hspace{1cm} (2)

Some values for \( A \) and \( B \) have been given by Tsurikova and Tsurkov [5] for various enclosed waters and Millero and Kremling [6] have shown that for the case of the Baltic the values of these "constants" can vary from location to location, and indeed from time to time.

**CHLORINITY AND ELECTRICAL CONDUCTIVITY**

Although the electrical conductivity of seawater had been used together with temperature for salinity determination since 1930 [7], precision salinometers based on this principle had to await the advent of modern electronics. Between 1955 and 1959 instruments utilizing a thermostatically controlled temperature bath were developed at the Woods Hole Oceanographic Institution, the University of Washington, and the National Institute of Oceanography (N.I.O., now the Institute of Ocean Sciences) in England, which gave results having standard deviations of about 0.005%o. By 1961 far more compact nonthermostated commercial instruments were available, employing an electronic compensation for the temperature difference between the seawater sample and that of the Copenhagen water used to standardize the instrument [8]. All the instruments gave conductivity ratios and temperatures which at that time were reduced to salinity using the results of Thomas, Thompson, and Utterback [9]. Cox [2] has noted that there was an error in their extrapolation of measured values to 15°C but even after this was corrected unacceptable discrepancies were occurring between salinities calculated from conductivity ratio and temperature and those resulting from the application of (1) to a chlorinity titration.

Once again, the International Council for the Exploration of the Sea suggested that an international commission be set up to look into the matter. The eventual response was a panel, sponsored by UNESCO, ICES, IAPSO, and SCOR, which first met in May 1962. In later years the terms of reference of the commission were somewhat expanded and it became known as the Joint Panel on Oceanographic Tables and Standards (JPOTS). The reports of the first two meetings of this body, which occurred in 1962 and 1963, have been re-issued as Appendices I and II of the report of the seventh meeting [10]; they make interesting reading. Cox and his co-workers at N.I.O. made comparisons between chlorinity, density, and the salinity derived from electrical conductivity ratio of many samples. For a given density or conductivity ratio, the chlorinity was found to vary up to 0.03%o. For a given density, the conductivity ratio varied only about 0.004%o equivalent chlorinity, which shows that density may be predicted from conductivity measurements with nearly an order better precision than from a chlorinity titration. As density values are the most important reason for making salinity measurements, this result clearly showed that the new methods of salinity determination were to be preferred in future work. The smaller scatter in the conductivity-density reading is due to the fact that conductivity measurements respond to any ion in solution, whereas chlorinity responds only to specific ions. Changes in the ionic content of seawater are thus corrected for in conductivity derived densities, at least in part, whereas an exchange of some ions in seawater materially affecting the density could leave the chlorinity unchanged.

JPOTS discussed the possibility of eliminating the concept of salinity from oceanography but concluded that this would be impractical, both for historical reasons and because the concept of salt content of seawater was very real to workers in fields such as biochemistry, where minor differences were immaterial and, for all practical purposes, salinity could be considered as conservative. It was concluded that for oceanographic purposes salinity must be redefined to make it a conservative property and then defined in terms of density. Specifically, the relationship

\[ S = 1.80655 \text{Cl} \]  \hspace{1cm} (3)

was suggested which is equivalent to (1) at \( S = 35%_o \). By determining the chlorinity and density of samples from the world's oceans and calculating a salinity from (3) above, salinity should be related to density arithmetically and the expression then be used as a definition of salinity. Salinity should also be related to conductivity ratio at 15°C and the measured values of the latter provide the accepted route to density.

Looked at with hindsight this series of recommendations suffered from the fact that still there was no method for coping with the varying chlorinity-salinity-density relationship under conditions of ionic change. Whereas (3) yielded one definition of salinity, the suggested salinity-density and salinity-conductivity ratio relationships would lead to others which would be mutually incompatible except for some specific set of ionic rations. The hope was that by taking a "mean-value" for the salinity-density interdependence an acceptable and useful scale could be produced. Major results based on these recommendations were published by Cox, Culkin, and Riley [11] and Cox, McCartney, and Culkin [12]. The former paper yielded an experimental relationship between chlorinity and the conductivity ratio of the sample at 15°C to that of standard Copenhagen seawater which was converted by (3) to yield

\[ S%_o = -0.08996 + 28.29729R_{15} + 12.80832R_{15}^2 -10.67869R_{15}^3 + 5.98624R_{15}^4 -1.32311R_{15}^5 \]  \hspace{1cm} (4)

where \( C(S, 15, 0) \) is the conductivity at 15°C, atmospheric pressure, of seawater of salinity \( S \) derived from (3) and \( C(35, 15, 0) \) is the conductivity of Copenhagen standard seawater. In the second paper the salinity "defined" by the relationship (4) was related to density by measuring the latter variable and electrical conductivity. In order to try and obtain "average" values of use in the real oceans, Cox and his co-workers had used natural waters only, or mixtures of natural...
water. For low salinities they had used Baltic samples, for higher salinities, Mediterranean and Red Sea samples. In the second paper mixtures of Red Sea and Baltic water were used to produce intermediary salinities. The whole accent was on acquiring information about “average” seawater and because of this Cox wished to relate the salinity to an absolute conductivity measurement rather than to a conductivity relative to Copenhagen water as given in (4), so as to be independent of any particular sample or ionic ratio as a reference. The new Copenhagen standard seawater was to be labeled with its absolute electrical conductivity as well as chlorinity. Using this water to calibrate the salinometer would then enable ratios to be computed and inserted into (4) to obtain salinity. Nevertheless, any difference between ionic ratios in the standard and the sample would still make (3) and (4) mutually incompatible.

The desire to make the standard independent of any particular store of water is highly commendable; and, looked at in retrospect, it was unfortunate that absolute conductivity was chosen as the basic property, as it is a very difficult quantity to measure and requires that the absolute dimensions of the test cell be known. As will be seen it is unnecessary to know the conductivity value of the standard; it is sufficient to know that it is constant. For this purpose it is possible to use a specific salt (for example, KCl) of adequate purity and use weighing as a means of obtaining it in fixed concentration solutions. Precision weighing is a well-established technique and accuracies of at least an order better than is required for the present purpose are available from a first class instrument. Precision balances are readily commercially available.

On the other hand, apparatus to measure the absolute conductivity at the required level of accuracy is presently available only at one institute only, where it was handmade, and it is most unlikely that it will see commercial production.

The work of Cox and his collaborators resulted in the publication of the International Oceanographic Tables [13] giving salinity as a function of conductivity ratio above 10°C and in the paper, “Redefinition of Salinity,” by Wooster, Lee, and Dietrich [14] representing SCOR, ICES, and IAPSO, respectively. They recommended the acceptance of a salinity as “defined” in (3) and (4), while the tables provided a basic set of data for use by oceanographers operating bench salinometers.

At the time that the International Tables were being published, commercially available in-situ salinometers were reaching operational status; an immediate problem arose. By far the greater portion of data recorded using these new instruments was at temperatures well below 10°C. How did one extrapolate conductivity ratios downward to lower temperatures? The best known study commissioned to answer this question was that of Brown and Allen tofts [15] conducted for the U.S. Office of Naval Research. They collected water samples from many parts of the world and defined 35%o seawater from any location as having a conductivity ratio of unity with 35%o Copenhagen water. This does not necessarily mean that the mass of salt per kilogram of solution would be the same in both cases, nor need there be any particular relationship between the chlorinities of the two samples. The investigators then diluted these samples by weight with distilled water or evaporated to produce weight defined salinities and proceeded to measure conductivity ratios as a function of temperature in the range 0-30°C. Quite apart from any questions of instrumental errors the results could not be exactly equivalent to those of Cox, Culkin, and Riley [11] and so originated a dichotomy in reporting salinity values.

Oceanographers with in-situ instruments used oceanographic bottles attached to the cast to collect water samples at the time of the measurement, which were subsequently analyzed in bench salinometers to provide calibration for the in-situ reading. For bench salinometer data it was internationally recommended that the UNESCO Oceanographic Tables should be used; for in-situ data it was impossible to use them, and Brown and Allen tofts’ results had to be invoked. The result was a series of forced marriages between the two data sets, none of which was truly satisfactory and even the best of these equations produced in attempts to resolve the conflict yielded salinities differing by up to 0.005%o for the same inputs in the oceanic range and up to 0.02%o in coastal waters [16], [17]. Equations were often the product of investigators having some particular regional interest, e.g., Perkin and Walker [18] and other users sometimes extended the range of parameters outside those recommended by the authors for their fit. A very real confusion existed and exists in the comparison of salinity data between major world oceanographic institutes. It was shown that even internal consistency was lacking for salinities from colder waters. Those calibrating in-situ instruments within a few degrees of freezing point found systematic salinity differences between their in-situ values and those derived from samples analyzed on the bench salinometer.

THE PRACTICAL SALINITY SCALE 1978

At the 1975 JOPTS meeting, this author was asked to prepare a background paper on the conversion of in-situ readings into salinities and this was eventually published as Lewis and Perkin [19], following an internal report version of the paper that had been circulated to a JOPTS membership in 1977. After a close examination of the problem it was concluded that a revision of the definition of salinity was necessary in order to eliminate ambiguities of greater magnitude than those associated either with the equations, or with instrumental error. The recommended redefinition is the Practical Salinity Scale 1978.

Lewis and Perkin concluded that there was no unique solution to the salinity problem but suggested that any useful definition 1) must be reproducible in any major laboratory throughout the world irrespective of the ionic content of local waters, 2) must be a conservative property, and 3) must allow density differences in any given water mass to be computed to acceptable limits.

It has already been pointed out that a “conductivity ratio” defined salinity scale is better than a “chlorinity” scale for density determination; and added to this is the study of Farland [20] showing that in the hands of average observers, titration is a less precise procedure than is con-
ductivity measurement. In order to eliminate the ambiguity exhibited by (3) and (4) under conditions of ionic ratio variation, the Practical Salinity Scale 1978 breaks the existing chlorinity-salinity tie in favor of a definitive salinity-conductivity ratio relationship; all waters of the same conductivity ratio then have the same salinity. A standard seawater of 35\%o practical salinity has by definition a conductivity ratio of unity at 15°C with a KCl solution containing a mass of 32.4356 g KCl in a mass of 1 kg of solution. In practice Merck "Suprapur" KCl has been found to be of adequate purity being consistent within a batch and between batches. It is worth noting that the major impurity is NaCl, and at the level of interest the molal conductivities of the two salts are sufficiently near to minimize the effect of the impurity.

To compute salinity from conductivity ratio

\[
S(\%_o) = a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} + a_4 K_{15}^2 + a_5 K_{15}^{5/2}
\]

\(a_0 = 0.0080\)
\(a_1 = -0.1692\)
\(a_2 = 25.3851\)
\(a_3 = 14.0941\)
\(a_4 = -7.0261\)
\(a_5 = 2.7081\)
\(\Sigma a_i = 35\)

2%o \(\leq S \leq 42%o\)

constitutes definition of Practical Salinity, where \(K_{15} = C(S, 15, 0)/C(KCl, 15, 0)\). \(C(S, 15, 0)\) is the conductivity of the sample, and \(C(KCl, 15, 0)\) is the conductivity of the standard KCl solution at 15°C atmospheric pressure (an unknown but fixed quantity). In practice it is necessary to use seawater rather than the KCl solution itself in order to standardize most bench salinometers as they include temperature compensation circuits, based on knowledge of the temperature coefficient of conductivity ratio, to allow for differences between the temperature of the standardizing solution and that of the sample. Insofar as this temperature coefficient is virtually the same for all natural seawater and that the temperature differences between sample and standard in the salinometer should not exceed 3°C any seawater having a conductivity ratio of unity at 15°C with the standard KCl solution can be used for \(C(KCl, 15, 0)\).

The values of the coefficients in (5) are based on experiments carried out on existing standard seawaters that were diluted and evaporated by weight. This ensures the conservatism of a salinity so defined and its local reproducibility. The particular set of ionic ratios used allows continuity with previous work, yet all seawaters will have their practical salinity computed using it, so that an electrical conductivity ratio will specify a salinity and a density irrespective of ionic content. The effect of this upon density calculations has been investigated by Lewis and Perkin [19] as far as the available data allows; it was shown that within the limits of experimental accuracy suitable for in-situ instruments densities of waters from locations other than the North Atlantic (the source of Copenhagen water) appeared to differ from that of North Atlantic water of the same practical salinity by a constant value depending on the source, over a wide salinity and temperature range (e.g., 0.035 in \(\sigma_T\) for Baltic waters). Differences of density were thus not affected by the densities themselves not being quite accurate. On the rare occasions when a density itself is needed reference would be made to a book of tables giving density corrections to be applied to that computed from a standard equation of state as a function of geographical position. The new Equation of State in terms of practical salinity values is reported on elsewhere. It is interesting to note that Millero [21] has demonstrated that the densities of water with the same absolute salinity are the same within experimental error. This is due to the fact that the molal volume of the various salts are not sufficiently different to affect density within the normal ranges of ionic contents of seawater.

REDUCTION OF DATA FROM IN-SITU CONDUCTIVITY/TEMPERATURE/DEPTH INSTRUMENTS

These instruments usually give the value of a conductivity ratio \(R\) for ambient water of salinity \(S\), temperature \(T\), at pressure \(p\) in relation to that of the standard KCl solution, or equivalent seawater standard at 15°C.

\[
R = \frac{C(S, T, p)}{C(35, 15, 0)} = \frac{C(S, T, p)}{C(S, T, 0)} \cdot \frac{C(S, T, 0)}{C(35, T, 0)} \cdot \frac{C(35, T, 0)}{C(35, 15, 0)} = R_p \cdot R_T \cdot R_r.
\]

from (5) \(C(35, 15, 0) = C(KCl, 15, 0)\).

Values for \(R_p\) were published by Brashaw and Schleicher [22] within the salinity range 31%o \(\leq S \leq 39\%o\) over a temperature range 0-25°C. Data acquired over the years using their equations has proven very good and the salinity differences between in-situ information acquired in this way and the corresponding bench salinometer analysis shows a Normal distribution [23]. During the latter half of 1978, Brashaw and Schleicher [24] extended their measurements on diluted standard seawater to include salinities down to 2%o and included a further set of measurements at 35%o so as to insure that both the new and old sets of data were comparable. At a meeting of the subcommittee of JPOTS at Woods Hole in January of 1979, their data was critically reviewed and their experimental procedures subjected to detailed scrutiny. Descriptions of the experiment, the data and fitting procedures for \(R_p\), as well as those of the other investigators measuring parameters used to calculate practical salinities and discussed below, are the subjects of other papers.
in this issue. Only the major salient facts will be related herein. A selection of Bradshaw and Schleicher's data was taken to cover the range of possible values to be met in the oceans and seas and the fit was made containing seven constants plus unity according to

\[ R_T = \frac{R}{r_T(1 + \alpha)} \]

i.e.,

\[ R_P = (1 + \alpha) \]

where

\[ \alpha = \frac{A_1 p + A_2 p^2 + A_3 p^3}{1 + B_1 T + B_2 T^2 + B_3 R + B_4 TR} \] (7)

The standard deviation was 1.3 ppm in salinity. Given \( R, T, \) and \( p, \alpha \) may be computed and the factor \( R_T r_T \) obtained. 

\( r_T \), the temperature coefficient of standard seawater was evaluated by Dauphinee et al. [25] in Ottawa and Poisson [27] in Paris, with supplementary measurements by Bradshaw and Schleicher [24] at Woods Hole and Millero in Miami. The first two investigators produced weight defined salinity samples by diluting or evaporating standard seawater. As evaporation is a somewhat doubtful procedure in that some salt may conceivably escape with the water, the technique used involved evaporation to an approximate salinity; then, after the measurements had been made, the sample was precisely diluted by weight to obtain a salinity below 35\%o so that an electrical conductivity measurement allowed its present salinity to be determined and its former salinity calculated. Bradshaw and Schleicher did not measure salinity by weight but recorded the change in conductivity ratio as a function of temperature, and this has been used as a check on a fit produced from a mixture of Dauphinee et al. and Poisson's data. The three data sets taken by three investigators in different countries using different apparatus showed a remarkable agreement. The maximum difference between the fit given below and Bradshaw and Schleicher's data within oceanographic ranges is about 0.0015 in salinity and the standard deviation of the fit is 0.00078 ppm. \( R_T \) is a function of both temperature and salinity and, quite surprisingly, it has been possible to separate these two variables to give

\[ S(\%o) = a_0 + a_1 R_T^{-1/2} + a_2 R_T + a_3 R_T^{3/2} + a_4 R_T^{-2} + a_5 R_T^{5/2} \]

\[ + \frac{(T - 15)}{1 + k(T - 15)} \{b_0 + b_1 R_T^{-1/2} + b_2 R_T + b_3 R_T^{3/2} + b_4 R_T^{5/2} \} \] (9)

\[ a_0 = 0.0080 \quad b_0 = 0.0005 \quad k = 0.0162. \]
\[ a_1 = -0.1692 \quad b_1 = -0.0056 \]
\[ a_2 = 25.3851 \quad b_2 = -0.0066 \]
\[ a_3 = 14.0941 \quad b_3 = -0.0375 \]
\[ a_4 = -7.0261 \quad b_4 = 0.0636 \]
\[ a_5 = 2.7081 \quad b_5 = -0.0144 \]
\[ \Sigma a_i = 35.0000 \quad \Sigma b_i = 0.0000 \]
\[ -2^\circ C < T < 35^\circ C \]

In all cases temperatures are measured according to the International Practical Temperature Scale (1968) (Comité International des Poids et Mesures [28]). It will be noted that (9) reduces to the definition (5) when \( T = 15^\circ C \).

Equations (7), (8), and (9) applied in sequence constitute the procedure to reduce in-situ CTD information.
DEFINITION OF THE PRACTICAL SALINITY SCALE 1978

1) Absolute salinity symbol \( S_A \) is defined as the ratio of mass of dissolved material in seawater to the mass of seawater. In practice this quantity cannot be measured directly and a practical salinity symbol \( S \) is defined for reporting oceanographic observations.

2) The practical salinity is defined in terms of the ratio of the electrical conductivity of the seawater sample at atmospheric pressure at 15°C to that of a KCl solution containing 32.4356 g of KCl in a mass of 1 kg of solution at the same pressure and temperature (International Practical Temperature Scale 1968). The ratio \( K_{15} \) defines practical salinity of the sample according to

\[
S(\%) = a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} + a_4 K_{15}^2 + a_5 K_{15}^{5/2}
\]

The values of the constants are given beneath (5).

SUPPLEMENTARY STATEMENT

The standard KCl solution has the same conductivity at 15°C as seawater from the North Atlantic of chlorinity 19.3740 \( \%_0 \) [29] - [31] and thus provides continuity with previous salinity scales. It was from measurements made on this water, diluted with distilled water or evaporated by weight, that the data giving rise to the above definition of salinity were obtained. Any oceanic water having a precisely known activity ratio of near unity at 15°C is henceforth to be regarded as a separate oceanographic instrument. All seawaters having the same constant variable in describing the properties of seawater.

REFERENCES

[30] F. Culkin and N. D. Smith, "Determination of the concentration of potassium chloride solution having the same electrical conductivity, at 15°C and infinite frequency, as standard seawater of salinity 35 000(\%_0) (chlorinity 19 3739(\%_0))," issue, pp. 22-23.