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Background papers and supporting data on the Practical Salinity Scale 1978

Unesco/ICES/SCOR/IAPSO
joint panel on oceanographic
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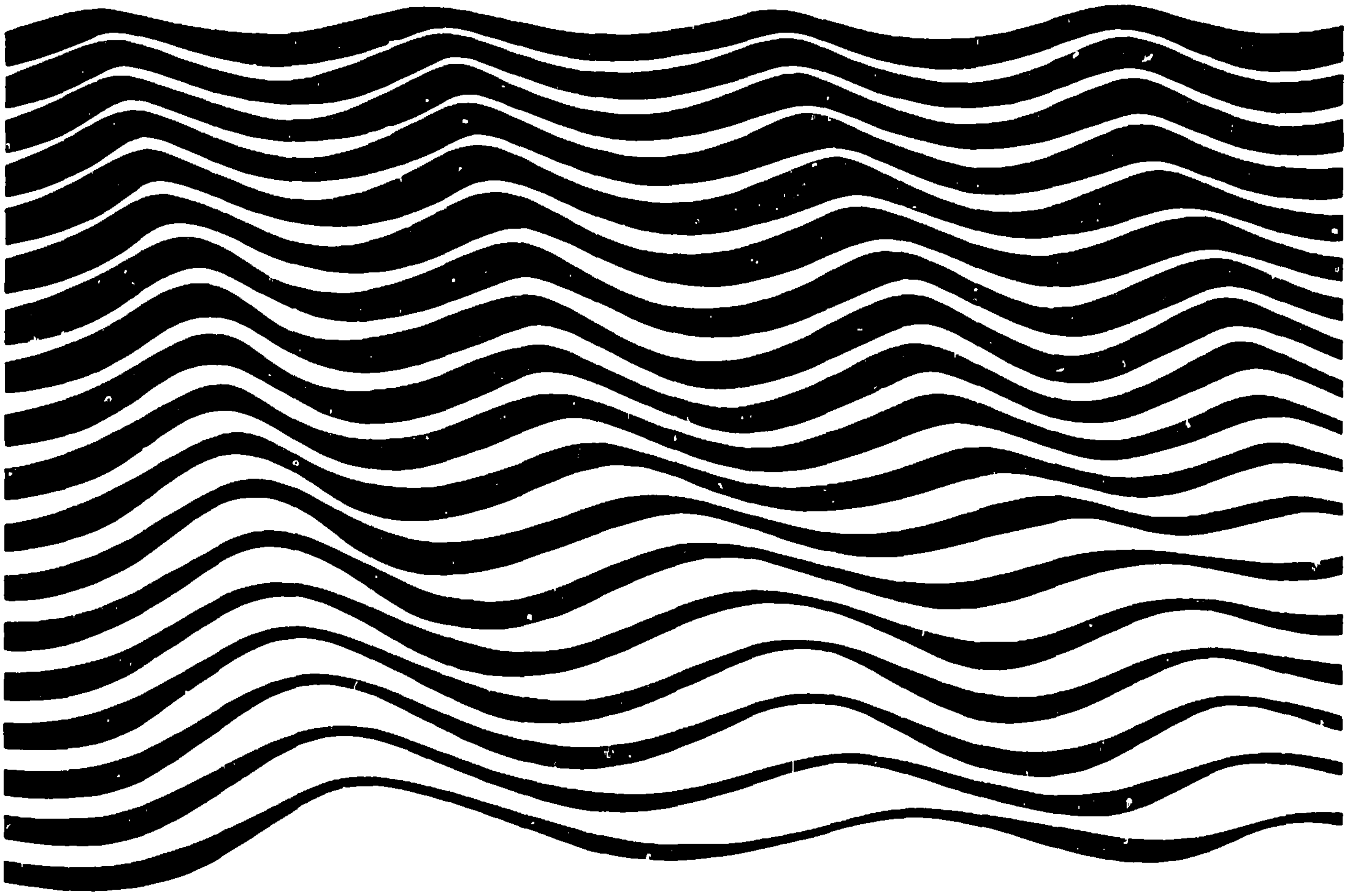

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33	Coastal lagoon research, present and future. Proceedings of a seminar, Duke University, August 1978. (Unesco, IABO). *To be published in English and French*	1981	-
34	The carbon budget of the oceans. Report of a meeting, Paris, 12-13 November 1979	1980	WG 62
35	Determination of chlorophyll in seawater. Report of intercalibration tests sponsored by SCOR and carried out by C.J. Lorenzen and S.W. Jeffrey, CSIRO Cronulla, N.S.W., Australia, September-October 1978	1980	
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Background papers and supporting data on the Practical Salinity Scale 1978

Unesco/ICES/SCOR/IAPSO
joint panel on oceanographic
tables and standards

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PREFACE

This series, the Unesco Technical Papers in Marine Science, is produced by the Unesco Division of Marine Sciences as a means of informing the scientific community of recent developments in oceanographic research and marine science affairs.

Many of the texts published within the series result from research activities of the Scientific Committee on Oceanic Research (SCOR) and are submitted to Unesco for printing following final approval by SCOR of the relevant working group report.

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[*] The pagination of this report itself is at the bottom of the page. The pagination of the original papers is at the top of the page.

GENERAL INTRODUCTION

In 1964, a panel of scientists were appointed jointly by Unesco, ICES, SCOR and IAPSO to advise on the establishment of international tables and standards. The first task of this Joint Panel on Oceanographic Tables and Standards (JPOTS) was the preparation of tables for computing salinity of seawater from determinations of electrical conductivity. Before these tables could be prepared, it was necessary to redefine salinity in terms of conductivity. After discussions (Unesco 1965), the JPOTS recommended (Unesco 1966,a) a definition of salinity based on determinations of chlorinity and conductivity on samples of natural seawater from all the oceans of the world. In October 1966, the "International Oceanographic Tables" (Unesco 1966,b) for computing salinity from conductivity, based on the above definition, were published. They include a tabulation of this definition at 15°C for salinities from 29 to 42°/oo, along with a correction table for measurements at temperatures other than 15°C, from 10 to 31°C.

However, the use of in situ measurements of conductivity for estimating salinity increased rapidly in the early seventies, rendering the "International Oceanographic Tables" unsuited for use in the majority of in situ measurements because the tables do not go below 10°C. Furthermore, a comparison of the conductivities of seven batches of standard seawater, relative to a KCl solution revealed that the conductivity of some batches was higher than that calculated from the certified chlorinity (Unesco 1976). This raised the problem of the calibration of the conductivity salinometers and CTD probes, as well as the definition of salinity itself. After discussion, the principle of calibrating standard seawater in electrical conductivity with a potassium chloride solution, was adopted and the establishment of a practical salinity scale was recommended by the JPOTS (Unesco 1978). Intensive work was then carried out in different laboratories with radically different measuring equipment. This resulted in considerable data on which are based the Practical Salinity Scale 1978, as well as the recommended algorithms for the calculation of practical salinity from the conductivity ratio at all temperatures and pressures over the range of oceanographic interest (Unesco 1979). This was finally adopted by the JPOTS during its meeting in Sidney, B.C., Canada, 1-5 September 1980 (Unesco 1981,a).

Whereas the previous salinity scale (Unesco 1966,b) was based on a conductivity-chlorinity relation using natural seawater, the Practical Salinity Scale 1978 is different in that the standard seawater used was diluted by weight with distilled water or evaporated to obtain other salinity values. This procedure was followed to ensure the constancy of composition of this seawater over the salinity range of interest. A precisely specified solution of potassium chloride was chosen as a reproducible electrical conductivity standard; an evaluation was then made of the concentration of this solution which yields a conductivity ratio of unity at 15°C with respect to a standard seawater (from the North Atlantic ocean) whose certified chlorinity was 19.3740°/oo, i.e. its salinity was exactly 35°/oo on the previous salinity scale. By convention, its practical salinity, on the new Practical Salinity Scale 1978, is 35, to ensure continuity at that salinity with the previous scale.

The following is a report on all the work and data on which both the Practical Salinity Scale 1978 and the algorithm for its calculation from in situ measurements are based. This report consists mainly of papers published in a special issue of the IEEE Journal of Oceanic Engineering and in Deep Sea Research, together with one unpublished paper. The cooperation of the publishers of both journals in granting permission for reproduction of these papers is greatly appreciated.

This report is divided into five sections and a conclusion :

- Outline of the work and the laboratories involved.
- Determination of the KCl solution primary electrical standard.
- Measurement of the conductivity ratio as a function of salinity, temperature and pressure.
- Fitting of the data.
- Conversion of the existing data.

In the Conclusion, the endorsed definition of the practical salinity scale, as drafted by the JPOTS at its last meeting (September 1980), is reported, together with the algorithm necessary for the calculation of practical salinity from the conductivity ratio at all temperatures and pressures over the ranges of oceanographic interest.

The Practical Salinity Scale 1978 was accepted by ICES in October 1979, by IAPSO in December 1979, by SCOR in September 1980 and by IOC of Unesco in June 1981. The new equations must be used for all values published on and after 1 January 1982.

New International Oceanographic Tables, Volume 3 (Unesco 1981,b) have been prepared and will be published shortly as Unesco Technical Papers in Marine Science No. 39. Copies are available, free of charge, upon request from

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France.

THE PRACTICAL SALINITY, 1978

DEFINITION

The practical salinity, symbol S, of a sample of seawater, is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15°C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32.4356×10^{-3}, at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds, by definition, to a practical salinity exactly equal to 35. The practical salinity is defined in terms of the ratio K_{15} by the following equation

$$S = 0.0080 - 0.1692\, K_{15}^{1/2} + 25.3851\, K_{15} + 14.0941\, K_{15}^{3/2} - 7.0261\, K_{15}^{2} + 2.7081\, K_{15}^{5/2}$$

formulated and adopted by the Unesco/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards, Sidney, B.C., Canada, 1 to 5 September 1980 and endorsed by the International Association for the Physical Sciences of the Ocean (IAPSO) in December 1979, the International Council for the Exploration of the Sea (ICES) in October 1979, the Scientific Committee on Oceanic Research (SCOR) in September 1980 and the Intergovernmental Oceanographic Commission (IOC) of Unesco in June 1981. This equation is valid for a practical salinity S from 2 to 42.

REFERENCES

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UNESCO 1979. Ninth Report of the Joint Panel on Oceanographic Tables and Standards, Paris, September 1978. Unesco Tech. Pap. in Mar. Sci., No. 30, p. 32.

UNESCO 1981,a. Tenth Report of the Joint Panel on Oceanographic Tables and Standards, Sidney, September 1980. Unesco Tech. Pap. in Mar. Sci., No. 36, p. 25.

UNESCO 1981,b. International Oceanographic Tables, Vol. 3. Unesco Tech. Pap. in Mar. Sci., No. 39 (in press).

OUTLINE OF THE WORK

AND THE LABORATORIES INVOLVED

Note on the symbols and units used in the Special Issue on the Practical Salinity Scale 1978 of the IEEE Journal of Oceanic Engineering

The papers presented in this report were published before the meeting of the Joint Panel on Oceanographic Tables and Standards, held in Woods Hole, USA, from 1 to 5 September 1980, during which time the definition of the Practical Salinity 1978, S, was established, and before the IAPSO General Assembly, held at Canberra, Australia, in December 1979. The symbol S(^{o}/oo) has been used in these papers for the practical salinity, instead of the adopted symbol S (Sun Report, 1980). The reader must read S instead of S(^{o}/oo) and thus ignore the "^{o}/oo" when they appear in the text regarding the practical salinity. For example, S(^{o}/oo) = 35.238 or S = 35.238^{o}/oo corresponds to S = 35.238.

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Introduction to the Special Issue on the Practical Salinity Scale 1978

THOMAS M. DAUPHINEE, SENIOR MEMBER, IEEE

***Abstract*—This paper outlines the work done at the five laboratories which provided, at the request of the Joint Panel on Oceanographic Tables and Standards (JPOTS), the basic data for the new Practical Salinity Scale 1978. Interlaboratory agreement of a very high order was achieved. The new scale is in process of acceptance by all major oceanographic societies, at which time it will be officially recommended for all future reporting of oceanographic data.**

THE PAPERS in this issue describe work that has been done very recently aimed at the development of a uniform repeatable Practical Salinity Scale, based on electrical conductivity measurements, for use by all oceanographers, both in the laboratory and in the field.

The work was undertaken at the request of the UNESCO-SCOR-ICES-IAPSO, Joint Panel on Oceanographic Tables and Standards (JPOTS) in several different laboratories with radically different measuring equipment. One of the conditions for acceptance of any results was that there should be independent confirmation over most of the range of interest.

As an aid to both internal and interlaboratory consistency it was decided that the measurements would be carried out on recent lots of standard seawater as supplied by the Seawater Service at the Institute of Oceanographic Sciences, Wormley, U.K., weight diluted or concentrated as necessary using distilled water for all dilutions. Deviations from the behavior of these solutions due to different origins of natural water are expected to be small and would be treated in the future as minor perturbations of the basic equations in the few cases where corrections were required.

The experimental work and mathematical analyses on which the Practical Salinity Scale 1978 is based were carried out at five different laboratories in four countries. The following groups were involved.

A. L. Bradshaw and K. E. Schleicher, Woods Hole Oceanographic Institution (WHOI), Woods Hole, MA.
F. Culkin and N. D. Smith, Institute of Oceanographic Sciences (IOS), Wormley, U.K.
T. M. Dauphinee, J. Ancsin, H. P. Klein, and M. J. Phillips, National Research Council (NRC), Ottawa, Ont., Canada.
R. G. Perkin and E. L. Lewis, Institute for Ocean Sciences (IOS-C), Sidney, B.C., Canada.
A. Poisson, Laboratoire d'Oceanographie Physique (LOP), Paris, France.

In addition important confirmatory evidence not actually used to derive the scale was obtained from Bradshaw and Schleicher, from Millero, University of Miami (U of M), Miami, FL, and from the earlier work of Brown and Allentoft (B-A), San Diego, CA.

THE MEASUREMENTS

The work done to develop the scale may be divided into six sections.

1) Set up a reproducible primary standard of electrical conductivity, against which all future lots of standard seawater and other secondary standards could be measured, and as close as possible to the conductivity of recent batches of standard seawater, so as to maintain continuity with previously reported data. The standard chosen was the conductivity at 15°C of a solution of potassium chloride (KCl) in distilled water having a specified concentration K_N chosen to give a conductivity ratio of 1 to current standard seawaters (referred to 35‰) at 15°C and normal atmospheric pressure. Determination of the standard concentration K_N and ancillary experiments to facilitate future work were carried out at IOS, NRC, and LOP. The standard seawater samples were supplied by the Standard Seawater Service at IOS and were known to be on the curve of conductivity (C) versus chlorinity (Cl) of recent batches, thus ensuring continuity of the scale at the transition date. Salinity was calculated from chlorinity using the accepted ratio $S = \mathrm{Cl} \times 1.806550$. It was agreed in advance by JPOTS that Merck "Suprapur" KCl suitably dried would be used for the KCl reference because it has excellent purity and a well-documented chemical analysis.

The agreement among the three laboratories turned out to be as good as one could reasonably expect. The final values for K_N (IOS 32.4353, NRC 32.4356, LOP 32.4358 gKCl/kg solution have a *spread* of only 0.5 mg/kg (equivalent to 0.6 ppm S)). The average (rounded to 32.4356 g/kg) has been used by JPOTS in the definition of the scale, as reported by Lewis in the paper immediately following entitled, "The Practical Salinity Scale 1978 and Its Antecedents."

2) Determine the relationship between salinity and the ratio $R_{S,15,0}$ of the conductivity at salinity S to the conductivity of standard seawater (35‰ exact) under identical conditions of 15°C and one atmosphere pressure (p (gauge) = 0).

3) Determine the variation with temperature of the ratio $R_{S,t,0}$ of conductivity at salinity S and temperature t to conductivity of standard seawater at the same temperature (p = 0).

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The author is with the National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6.

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The measurements for 2 and 3 above were carried out over the whole ocean range at NRC ($0 < S < 42‰$, $-2 < t < 35°C$) and LOP ($4 < S < 42‰$, $-1 < t < 30°C$) and confirmatory data was supplied by WHOI (see 4) below), U of M and B-A. The NRC and LOP data are in total agreement over almost the entire range of overlap to the 1-ppm level, and are with few exceptions within the combined experimental error of the confirmatory data. The few major divergences from the earlier (B-A) data were confirmed by WHOI and, very fortunately, are in areas infrequently encountered in ocean measurements so that the many past calculations of salinity based on this part of their work are not likely to be significantly affected.

4) Determine the effect of temperature on the ratio r_t of conductivity of standard seawater ($35‰$ S) at temperature t to its 15°C value ($C_{35,t,0}/C_{35,15,0}$): The function r_t is required for most *in-situ* measurements where the measured quantity is the ratio of *in-situ* conductivity to the conductivity at $35‰$, some reference temperature, usually 15°C and $p = 0$. These measurements were carried out at NRC and WHOI with confirmation from earlier work at NRC. The WHOI data lies between the two NRC sets and differs from the most-recent more-accurate set by substantially *less* than 1 ppm S, except at the highest temperatures. The new equation is significantly different from the previous B-A equation, particularly at high and low temperatures, and may lead to recalculation of some of the earlier data where the precision of measurement warrants it.

The WHOI measurements of the equivalent ratio at other salinities $r_{s,t} = C_{s,t,0}/C_{s,15,0}$ also supplied important confirmatory data for 3) above.

5) Determine the effect of pressure on the conductivity of seawater over the full range of oceanic temperatures and salinities. This function is required to correct *in-situ* conductivity measurements to their zero pressure equivalent before the final calculation of the salinity is carried out. Equipment to measure conductivities under pressure to the accuracy required was only available at WHOI, and so all measurements were carried out there and it was not possible to get good independent confirmation of the Bradshaw and Schleicher data. However, confirmation was available from their earlier, almost universally used pressure data, since the new and old data sets are in excellent agreement. Also field checks by other workers have indicated there are no problems with the earlier data. The new equations are based on both sets of measurements.

6) Consolidate into a single set of equations the final experimental values as supplied by the various laboratories. These equations define Practical Salinity in terms of the conductivity ratio at 15°C and give a mechanism for calculation of salinity from conductivity, temperature, and pressure measurements at any temperature or pressure in the ocean range.

This part of the work was carried out at IOS-C as a "neutral party" not involved in the actual measurements, with suggestions as to appropriate forms of the equations from the groups involved and some check calculations at NRC. The outcome of this analysis has been a set of equations quite different in form from those previously in use which were shown to be inadequate to match the precision of the new experimental data base. These equations have been accepted by the groups involved and by JPOTS and were adopted by a large part of the International Oceanographic Community at the IAPSO meeting in Canberra, Australia, in December of 1979. They are recommended for use by all oceanographers in reporting future oceanographic data. A set of oceanographic tables based on these equations, to replace the older version which was based on the work of Cox, Culkin, and Riley will shortly be available as a UNESCO publication.

CONCLUSION

The papers in this issue, therefore, contain the whole body of information on which the new Practical Salinity Scale 1978 is based. Because of the great importance of the new scale to instrumentation and measurement in the ocean and the long time over which the scale is expected to be used, your Editors have felt justified in devoting an entire issue to the subject. We hope that oceanographers everywhere will seize the opportunity now presented to have completely consistent reporting of ocean salinity data.

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The Practical Salinity Scale 1978 and Its Antecedents

EDWARD LYN LEWIS

***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 simple 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

$$S\text{‰} = 0.03 + 1.805\ \mathrm{Cl}\text{‰} \tag{1}$$

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 0.3285234 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 0.0‰ chlorinity one is left with 0.03‰ 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

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The author is with the Frozen Sea Research Group, Institute of Ocean Sciences, P. O. Box 6000, 9860 W. Saanich Rd., Sidney, B. C., Canada V8L 4B2.

is a particular example of general equation

$$S = A + B\,\mathrm{Cl}. \tag{2}$$

Some values for A and B have been given by Tsurikova and Tsurikov [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‰. 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 reissued as Appendixes 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‰. For a given density, the conductivity ratio varied only about 0.004‰ 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

$$S = 1.80655\,\mathrm{Cl} \tag{3}$$

was suggested which is equivalent to (1) at $S = 35‰$. 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

$$S‰ = -0.08996 + 28.29729R_{15} + 12.80832R_{15}^2 - 10.67869R_{15}^3 + 5.98624R_{15}^4 - 1.32311R_{15}^5 \tag{4}$$

$$R_{15} = C(S, 15, 0)/C(35, 15, 0)$$

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 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 Allentoft [15] conducted for the U.S. Office of Naval Research. They collected water samples from many parts of the world and defined 35‰ seawater from any location as that having a conductivity ratio of unity with 35‰ 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 Allentofts' 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‰ for the same inputs in the oceanic range and up to 0.02‰ 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 JPOTS 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 JPOTS 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 conductivity 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‰ practical salinity has by definition a conductivity ratio of unity at 15°C with a KCl solution containing a mass of 32.4356 gKCl 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

$$
\begin{aligned}
S(‰) &= a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} \\
&\quad + a_4 K_{15}^{2} + a_5 K_{15}^{5/2} \qquad (5)
\end{aligned}
$$

$$a_0 = 0.0080$$

$$a_1 = -0.1692$$

$$a_2 = 25.3851$$

$$a_3 = 14.0941$$

$$a_4 = -7.0261$$

$$a_5 = 2.7081$$

$$\Sigma a_i = 35$$

$$2‰ \leq S \leq 42‰ .$$

constitutes definition of Practical Salinity, where $K_{15} = C(S, 15, 0)/C(\mathrm{KCl}, 15, 0)$. $C(S, 15, 0)$ is the conductivity of the sample, and $C(\mathrm{KCl}, 15, 0)$ 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. Inasfar 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 $C(\mathrm{KCl}, 15, 0)$.

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 σ_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.

$$
\begin{aligned}
R &= \frac{C(S, T, p)}{C(35, 15, 0)} \\
&= \frac{C(S, T, p)}{C(S, T, 0)} \cdot \frac{C(S, T, 0)}{C(35, T, 0)} \cdot \frac{C(35, T, 0)}{C(35, 15, 0)} \\
&= R_p \cdot R_T \cdot r_T. \qquad (6)
\end{aligned}
$$

from (5) $C(35, 15, 0) = C(\mathrm{KCl}, 15, 0)$.

Values for R_p were published by Bradshaw and Schleicher [22] within the salinity range $31‰ \leq S \leq 39‰$ 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, Bradshaw and Schleicher [24] extended their measurements on diluted standard seawater to include salinities down to 2‰ and included a further set of measurements at 35‰ 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

$$\alpha = \frac{A_1 p + A_2 p^2 + A_3 p^3}{1 + B_1 T + B_2 T^2 + B_3 R + B_4 TR} \tag{7}$$

and

$$\begin{aligned}
A_1 &= 2.070 \times 10^{-5}\\
A_2 &= -6.370 \times 10^{-10}\\
A_3 &= 3.989 \times 10^{-15}\\
B_1 &= 3.426 \times 10^{-2}\\
B_2 &= 4.464 \times 10^{-4}\\
B_3 &= 4.215 \times 10^{-1}\\
B_4 &= -3.107 \times 10^{-3}.
\end{aligned}$$

The standard deviation was 1.3 ppm in salinity. Given R, T, and p, α 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 Bradshaw and Schleicher [24] at Woods Hole. The former investigators extended and refined the measurements reported by Dauphinee and Klein [26]. The comparison in the two sets of data taken by different investigators at different locations using different apparatus is quite remarkable. Both sets of data were used to produce the fit

$$r_T = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4 \tag{8}$$

$$\begin{aligned}
c_0 &= 6.766097 \times 10^{-1}\\
c_1 &= 2.00564 \times 10^{-2}\\
c_2 &= 1.104259 \times 10^{-4}\\
c_3 &= -6.9698 \times 10^{-7}\\
c_4 &= 1.0031 \times 10^{-9}
\end{aligned}$$

which has a deviation of 8.20×10^{-6} in r_T equivalent to a salinity of about 0.0004‰. Comparison between the results of Dauphinee and Klein [26] and Brown and Allentoft [15] shows the source of the problem already noted in reduction of *in-situ* conductivity/temperature/depth readings near freezing point; there is a difference equivalent to about 0.0085‰ salinity at 0°C between the measurements. We conclude that there was some experimental error in Brown and Allentoft's investigation.

R_T was measured 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‰ 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 0.0007‰. R_T is a function of both temperature and salinity and, quite surprisingly, it has been possible to separate these two variables to give

$$\begin{aligned}
S(‰) = {} & a_0 + a_1 R_T^{1/2} + a_2 R_T + a_3 R_T^{3/2} \\
& + a_4 R_T^2 + a_5 R_T^{5/2} \\
& + \frac{(T-15)}{1+k(T-15)}\{b_0 + b_1 R_T^{1/2} + b_2 R_T + b_3 R_T^{3/2} \\
& + b_4 R_T^2 + b_5 R_T^{5/2}\}
\end{aligned} \tag{9}$$

$$\begin{array}{lll}
a_0 = 0.0080 & b_0 = 0.0005 & k = 0.0162.\\
a_1 = -0.1692 & b_1 = -0.0056 & \\
a_2 = 25.3851 & b_2 = -0.0066 & \\
a_3 = 14.0941 & b_3 = -0.0375 & \\
a_4 = -7.0261 & b_4 = 0.0636 & \\
a_5 = 2.7081 & \underline{b_5 = -0.0144} & \\
\Sigma a_i = 35.0000 & \Sigma b_i = 0.0000 & \\
-2°\mathrm{C} \leq T \leq 35°\mathrm{C} & &
\end{array}$$

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 $T = 15°$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

$$S(^o/_{oo}) = a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} + a_4 K_{15}^{2} + a_5 K_{15}^{5/2}.$$

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 $^o/_{oo}$[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 conductivity ratio of near unity at 15°C with the standard KCl solution is a secondary standard for everyday calibration of oceanographic instruments. All seawaters having the same conductivity ratio have the same practical salinity, and chlorinity is henceforth to be regarded as a separate independent variable in describing the properties of seawater.

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DETERMINATION OF THE KCl SOLUTION

PRIMARY ELECTRICAL STANDARD

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The Effect of Concentration and Temperature on the Conductivity Ratio of Potassium Chloride Solutions to Standard Seawater of Salinity 35‰ (Cl 19.3740‰)

THOMAS M. DAUPHINEE, SENIOR MEMBER, IEEE, JOHN ANCSIN, H. PETER KLEIN, AND M. JOHN PHILLIPS

Abstract—**The ratios $Z_{K,t}$ of electrical conductivities of potassium chloride (KCl) solutions of known concentration (K) to standard seawater at the same temperature have been measured at 15°C and 24°C for solutions with $Z_{K,15}$ between 0.96 and 1.04. The "normal" concentration (N or K_N) giving $Z_{N,15} = 1$ was found to be $K_N = 32.4356$ gKCl/kg solution. The effect of temperature on $Z_{N,t}$ was measured over the range 15°C to 30°C. Equations are given for KCl concentration as a function of Z_{15} and the inverse function, for Z_{15}/Z_{24} as a function of Z_{24} (to allow use of a laboratory salinometer for the KCl-seawater comparisons), and $Z_{N,t}$ as a function of temperature.**

INTRODUCTION

IN THE PROPOSED new Practical Salinity Scale [1], the ultimate reference for standard seawater will be the electrical conductivity at 15° of a potassium chloride (KCl) solution of known concentration, the concentration being chosen to maintain continuity with salinities based on the previous fixed ratio (1.80655) [2] between salinity and chlorinity. We have carried out measurements of the conductivity ratio $Z_{K,t}$ of KCl solutions to standard seawater P79 (at the same temperature and corrected to exactly 35‰) at a number of concentrations (K) giving conductivity ratios from 0.96 to 1.04 at 15°C. From this data we have derived equations relating $Z_{K,15}$ and $Z_{K,24}$ to gKCl/kg solution and we have determined the "normal" KCl concentration (N or K_N) having a conductivity ratio $Z_{N,15} = 1$ at 15°C. $K_N = 32.4356$ g/kg.

In addition, as a convenience to those who might wish to make the KCl comparison at normal room temperatures, we have measured the variation of $Z_{N,t}$ at 3°C intervals from 15°C to 30°C and derived an equation relating $Z_{N,t}$ to temperature. This allows the KCl-seawater comparison to be carried out at any convenient temperature with a laboratoy salinometer and facilitates correction back to an exact temperature if the actual measurement temperature deviates somewhat from the ideal.

This work was carried out at the request of the Joint Panel on Oceanographic Tables and Standards (JPOTS) [1] concurrently with measurements by Poisson [3] and Culkin and Smith [4] (both in this issue). A more detailed description of these measurements will be given later in a UNESCO technical paper.

PREPARATION OF KCl SOLUTIONS

Accurately known concentrations of KCl were prepared in ampoules suitable for our conductivity measuring system as follows. The process started with samples of ultra pure Merck KCl. This was originally from one lot to be used by all groups involved in the measurements. But later, as confirmation that the particular lot made no difference, the samples were made from several different lots with identical results: and, in the final measurements, no distinction was made, except to assure that a number of lots were represented.

Residual water was driven off by heating the KCl in a crucible in air for a period of time. Originally the heating was carried out at about 110°C, 150°C, and 200°C for up to 24 h. Subsequent measurements indicated, however, that this was not sufficient and the final measurements were based on heating in bulk form as received, to at least 260°C for a number of hours, or fusing the KCl. The fusion process used is very simple and, we believe, preferable because it is fast and gives smaller scatter. The KCl was heated with an oxygen gas flame in a platinum crucible until it melted. It was then poured from the crucible onto a clean polished stainless steel plate about 0.5 cm thick on which it froze, without sticking, into numerous lumps of very convenient size and rapidly cooled to room temperature. Sticking was prevented by a thin layer of KCl powder which forms by condensation on the plate and prevents actual contact between the lumps and the steel. Poisson (private communication) has confirmed that the lumps retain the original purity and that even the powder (which we do not use anyway) is barely contaminated.

Re-hydration of the desiccated granular KCl during cooling and weighing has been shown by timed series of successive weighings to be completely negligible. Even keeping the desiccated KCl in an atmosphere of 100-percent RH at 22°C resulted in only 30 ppm mass gain in 24 h, equivalent to an error of only 0.001 g/kg in our KCl concentration calculations.

For weighing, a suitable amount of dried KCl was placed on a light stainless steel weighing pan with a pourspout (as recommended by Culkin and Smith, private communication) and its mass was determined from weighings of the pan plus KCl and pan plus residual KCl, respectively, before and after the KCl lumps were poured into a glass bottle. The appropriate balance weight and air buoyancy corrections were made using a KCl density of 1.984 g/cm^3. The bottle was

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The authors are with the Division of Physics, National Research Council of Canada, Ottawa, Ont., Canada K1A OR6.

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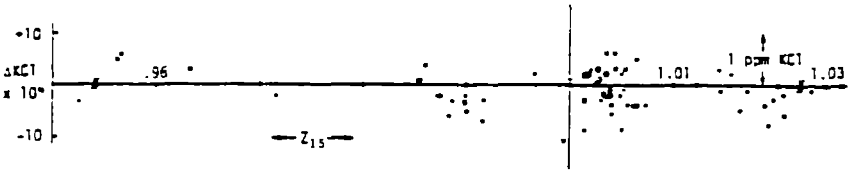

Fig. 1. The differences $\Delta K = K_C - K_W$ for the solutions made from KCl dried at 200°C(·), 260°C(*x*), and by melting (*o*). K_C is the concentration calculated from Z_{15} and (2), K_W is calculated from dilution ratios obtained by weighing.

then filled with distilled water to make a stock solution approximately four times more concentrated than the desired 32 g/kg. After all of the salt lumps had been dissolved to a uniform solution, the mass of solution was determined using the established tables for the density of KCl solutions, and the concentration was then calculated from mass of KCl/mass of solution. This "stock" solution was then used to make up a range of solutions of the desired salinities (in ampoules made from standard seawater ampoules) within a narrow range around 32 g/kg, using a dilution technique which has been described elsewhere in detail [3], [5]. Briefly, it consists of adding distilled water through a fine tube, driven by air pressure, to a pre-weighed ampoule with a narrow opening to prevent evaporation. After thermal equilibrium is achieved and the air inside is saturated with water vapor, the mass of liquid water is determined by weighing, with appropriate density corrections for the presence of vapor. A cap with a fine pressure equalizing hole limits evaporation during weighing. The appropriate amount of stock solution of known salinity is then added in the same way, without danger of evaporation because the air is saturated. The final weighing then allows calculation of the salinity.

THE CONDUCTIVITY MEASUREMENTS

The measurements of conductivity were carried out with the same apparatus used to measure the effect of concentration and temperature on the conductivity of seawater [5], [6]. The sample bottle, prepared as described above, was first sealed with a flat neoprene sheet pressed across the end and shaken vigorously to assure good mixing. It was then placed in the measuring system where the solution was driven by air pressure into the two heat exchangers and cells in parallel, one at close to 15°C and the other at some other chosen temperature. After a number of flushes four or six readings were taken on each cell, with a flush after each two readings, along with periodic readings of the temperatures of the two baths. At frequent intervals one lot of standard seawater was run through to check that there had been no change of effective cell constant.[1] The cell constant used to represent standard seawater was the average of these readings since experience has shown that our cell constant does not drift significantly over short periods of time.

Sets of readings over a range of concentrations bracketing $Z_{15} = 1$ were taken with the two baths at 15°C and 24°C, respectively. As mentioned earlier, we started by making the solutions from KCl as purchased air dried for about 24 h at between 120° and 150°C, but were unable to get consistent results and, therefore, raised the drying temperature progressively to 200°C, then 260°C, and finally to the melting point.

THE DETERMINATION OF K_N

The data from the 200°C solutions were quite consistent and covered a suitably wide range of concentrations. They were used to develop a second degree equation expressing the concentration K as a function of $\Delta Z_{K,15} = (Z_{K,15} - 1)$ i.e.,

$$K(\text{g/kg}) = a + b(\Delta Z_{K,15}) + c(\Delta Z_{K,15})^2. \qquad (1)$$

The definitive set of readings was then taken with samples having concentrations near the "normal" concentration made from KCl dried at 260°C and from the fused salt. For comparison purposes, a set with salt dried at 150°C was taken as well.

The constant term of (1) was then adjusted slightly downward (by -2×10^{-4} g/kg) to make the concentration equation pass through the average of the 260°C and fused-salt set. The "normal" concentration K_N is defined as the concentration having a conductivity equal to that of standard seawater of exactly 35‰ salinity (chlorinity 19.37395‰) and 15°C, that is, $Z_{N,15} = 1$ In our case Lot P79 was used as the reference (Cl = 19.3760‰). A large number of ampoules of this lot were supplied to us for the purpose by the Standard Seawater Service (at I.O.S., Wormley, U.K.). Our final value was $K_N = 32.4356$ g/kg.

For concentrations near K_N (± 1.5 g/kg) the expression relating concentration (K) and Z_{15}, is where $\Delta Z_{15} = Z_{15} - 1$ and $\Delta K = (K - 32.4356)$;

$$K = 32.4356 + 33.6484\,(\Delta Z_{15}) + 0.3968\,(\Delta Z_{15})^2 \qquad (2)$$

$$Z_{K,15} = 1 + 0.029719\,(\Delta K) - 0.0000104(\Delta K)^2. \qquad (2a)$$

Table I gives the results of our measurements on the samples dried at 200 +°C. After a slight adjustment for measuring temperature (see (4) later) the value obtained for $K_{N,15}$ was 32.4358 g/kg, only 2×10^{-4} g/kg above our final value.

Table II gives the results of our definitive set using KCl dried at 260°C and the fused salt. The standard deviation from (2) is 3.6×10^{-4} g/kg, but it will be seen that signi-

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[1] By "cell constant" we mean the conductance reading in bridge units for standard seawater of exactly [illegible] salinity, at either 15°C or the measurement temperature, as appropriate.

TABLE I
THE RESULTS OF MEASUREMENTS ON SAMPLES MADE FROM KCl DRIED AT 200 + °C

$Z_{15.0320}$	K_w***	K_c	$\Delta(K) \times 10^4$	
1.004872	32.5999	32.5998	-1	
.991699	32.1567	32.1566	-1	
.987439	32.0133	32.0133	0	
1.019382	33.0886	33.0882	-4	
.991500	32.1504	32.1499	-5	
1.007524	32.6893	32.6891	-2	
1.003978	32.5701	32.5698	-3	
1.017284	33.0179	33.0176	-3	
.989914	32.0967	32.0966	-1	
1.039710	33.7730	33.7727	-3	
1.018760	33.0675	33.0673	-2	
1.005362	32.6162	32.6163	+1	
1.004943	32.6030	32.6022	-8	
.988174	32.0384	32.0380	-4	
1.019839	33.1051	33.1036	-15	*
1.018807	33.0695	33.0689	-6	
1.002934	32.5347	32.5346	-1	
.989867	32.0953	32.0950	-3	
.971757	31.4846	31.4859	+13	*
1.004570	32.5888	32.5897	+9	*
1.034073	33.5815	33.5829	+14	*
1.061129	34.4941	34.4943	+2	
1.001407	32.4839	32.4832	-7	
.942642	30.5073	30.5072	-1	
1.020464	33.1247	33.1246	-1	
1.005139	32.6084	32.6088	+4	
.988770	32.0582	32.0581	-1	
.996207	32.3079	32.3083	+4	
1.012273	32.8487	32.8489	+2	
1.028410	33.3921	33.3922	+1	
1.015561	32.9592	32.9596	+4	
1.002015	32.5032	32.5037	+5	
.985162	31.9364	31.9367	+3	
.989904	32.0962	32.0962	0	
1.005719	32.6285	32.6284	-1	
1.019768	33.1013	33.1012	-1	
.985572	31.9502	31.9505	+3	
1.006664	32.6594	32.6602	+8	
1.014629	32.9281	32.9282	+1	
1.014349	32.9183	32.9188	+5	
1.002998	32.5366	23.5368	+2	
.987251	32.0070	32.0078	0	
1.033300	33.5566	33.5568	+2	
1.017278	33.0173	33.0174	+1	
1.000072	32.4380	32.4383	+3	
.986103	31.9677	31.9684	+7	
.971649	31.4820	31.4820	0	
1.000000		32.4359		**

* Not used for fit. Standard deviation = 3.6 × 10^{-4} g/kg.

** 32.4358 after correction to 15°C. *S* reference is standard water P79.

*** K_c and K_w are the concentrations obtained from conductivity measurements (Z_{15} and (2)) and weight dilution, respectively.

ficantly lower scatter ($\sigma = 1.9 \times 10^{-4}$ g/kg) is obtained with the fused salt. We recommend its use.

Fig. 1 shows a plot of all data for 200°C and above versus (2).

Table III gives the deviations of our final ≈150°C drying set. These samples were made in groups of three from four different dryings and different lots of Merck KCl. It is obvious that serious errors in stock solution concentrations have resulted from insufficient drying of the KCl.

Table IV gives the conductance readings *R* of the standard seawater on which the reference to seawater lot P79 was made during the definitive set of readings. Deviations ($\Delta R/R$, ΔS) from the average are also given. Reproducibility of these readings is discussed later.

TABLE II
THE RESULTS OF THE MEASUREMENTS ON SAMPLES MADE FROM KCl DRIED AT >250°C AND FUSED KCl*

Z_{15}	K_w	K_c	$\Delta(K) \times 10^4$
Fused			
1.002720	32.5720	32.5271	+1
1.001849	32.4976	32.4978	+2
1.002649	32.5247	32.5247	+0
1.001866	32.4982	32.4984	+2
1.002789	32.5291	32.5294	+3
1.003439	32.5511	32.5513	+2
1.003323	32.5476	32.5474	-2
1.003885	32.5664	32.5663	-1
1.003785	32.5632	32.5630	-2
Dried at 250 + °C			
1.001354	32.4815	32.4812	-3
1.003680	32.5596	32.5594	-2
1.004176	32.5765	32.5761	-4
1.005290	32.6133	32.6136	+3
.999539	32.4212	32.4201	-11
1.003498	32.5527	32.5533	+6
.963134	31.1954	31.1957	+3
.956283	30.9649	30.9654	+5
.956973	30.9881	30.9895	+4
1.004863	32.5989	32.5992	+3
1.006428	32.6513	32.6519	-4
1.004329	32.5807	32.5813	+6

* Symbols as in Table I. Three different lots of Merck "SUPRAPUR" KCl are represented.

TABLE III
ERRORS IN KCl WEIGHT CALCUALTIONS AFTER AIR DRYING AT APPROXIMATELY 150°C*

	$\Delta(K) \times 10^4$		$\Delta(K) \times 10^4$
Lot 1	-65	Lot 3	-14
	-63		-14
	-64		-16
Lot 2	-26	Lot 4	-36
	-23		-40
	-23		error

* Symbols as in Tables I and II. The samples in each lot are made from the same stock solution, but each lot is from a different batch of Merck "SUPRAPUR" KCL.

TABLE IV
THE STANDARD SEAWATER CONDUCTANCE READINGS (*R*) ON WHICH K_N IS BASED (AT 15°C) AND THE CORRESPONDING 24°C READINGS*

	15°C			24°C		
	Cell D	$\frac{\Delta R}{R} \times 10^6$	$\Delta S \times 10^4$	Cell C	$\frac{\Delta R}{R} \times 10^6$	$\Delta S \times 10^4$
79/5/24	79.1558	- 1	0	94.4566	-5	-2
	79.1570	+14	6	94.4584	14	6
	79.1555	- 5	-2	94.4567	-4	-2
79/5/25	79.1555	- 5	-2	94.4567	-4	-2
	79.1560	+ 1	0	94.4574	+3	1
	79.1555	- 5	-2	94.4566	-5	-2
79/5/30	79.1565	+ 8	3	94.4577	+6	2
	79.1563	+ 5	2	94.4574	+3	1
	79.1553	- 6	-3	94.4566	-5	-2
	R_{AV} = 79.1559 (P79.)			R_{AV} = 94.45712 (P79.)		
	R_{STD} = 79.14841			R_{STD} = 94.44818		
	P79. Cl = 19.3760‰; S = 35.0037‰					

* Z_{15} = 1 at R_K = 79.14841. *R* = 100 represents a cell conductance of 4000 μmho. ΔR = (*R*-*R* average). ΔS is the equivalent in salinity units.

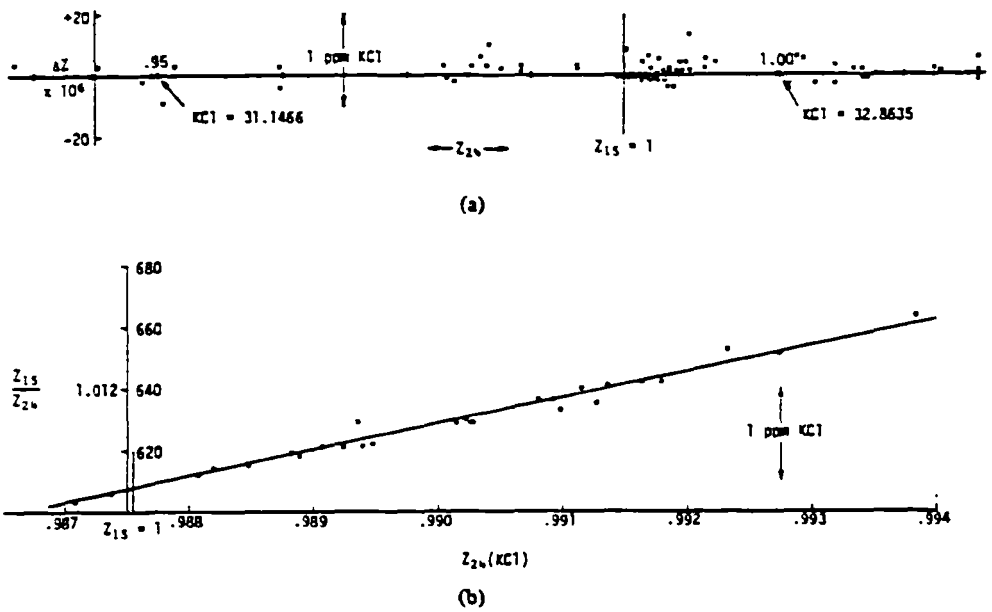

Fig. 2. The effect of concentration on the ratio Z_{15}/Z_{24}. (a) Deviations (ΔZ) of all measured values from (3). (b) Measured values of Z_{15}/Z_{24} plotted on expanded scale of Z_{24} for the final set of measurements (260°C and fused).

THE EFFECT OF TEMPERATURE ON $Z_{N,t}$

By combining all of our 15°C and 24°C data we have also derived an expression (conveniently linear) for the ratio $(Z_{15}/Z_{24})_K$ which allows Z_{15} to be calculated with great precision, for use in (2), from similar measurements at 24°C (Z_{24}) made with a laboratory salinometer. Since the equation does not require a knowledge of the KCl concentration it was permissible to use all available ratios, including those with less than ideal drying, and a total of 83 data points were represented. The 24°C to 15°C conversion equation fits the data with a standard deviation of $\sigma = 3.5 \times 10^{-6}$ (1.2×10^{-4} g/kg) and has the form

$$Z_{15}/Z_{24} = 1.004217 + 8.4968 \times 10^{-3} Z_{24} \tag{3}$$

or, in terms of deviation from the standard value $Z_{N,24} = 0.987550$

$$Z_{15}/Z_{24} = 1.012608 + 8.4968 \times 10^{-3}(Z_{24} - 0.987550). \tag{3a}$$

Fig. 2(a) shows a plot of the measured values of Z_{15}/Z_{24} versus (3).

Fig. 2(b) is an expanded plot of the points near $Z_{15} = 1$ for the final group of readings (>250°, and fused salt) which were used to fix the intercept $Z_{N,24} = 0.987550$ at the "normal" concentration ($Z_{N,15} = 1$).

TABLE V
THE EFFECT OF TEMPERATURE ON $Z_{N,t}$*

t°C	Z_t/Z_{15}	$\Delta Z_t \times 10^6$	$\Delta K \times 10^4$
15	1.000000	+5	+2
18	.995685	-3	-1
21	.991535	-3	-1
24	.987548	-3	-1
27	.983725	+4	+2
30	.980065	-9	-4

* $\Delta Z_{N,t} = Z_{N,t}$ (measured) − $Z_{N,t}$ (calculated from (3)). ΔK is the equivalent KCl concentration difference. Each $Z_{N,t}$ is the average of two KCl measurements.

In addition to the 24°C data a series of measurements were made alternately on KCl solutions very near the normal concentration and on standard seawater with the variable bath close (±<0.001°C) to 15°, 18°, 21°, 24°, 27°, and 30°C and the reference bath at 15°C. The variation of $Z_{N,t}$ could be expressed very accurately by a second degree equation in

$$\Delta t = (T - 15°\mathrm{C})$$

$$Z_{N,t} = 1 - 1.4655 \times 10^{-3}(\Delta t) + 9.103 \times 10^{-6}(\Delta t)^2, \quad -1 < \Delta t < 15°\mathrm{C}. \tag{4}$$

Equation (4) is not very sensitive to variations of concentration about the standard value. The experimental values obtained and deviations from (4) are given in Table V and plotted in Fig. 3. The function

$$g_{N,t} = \frac{dZ_{N,t}}{dt} + Z_{N,t}\frac{dr_t}{dt}$$

where r_t is the previously determined [5], [6] temperature effect function for standard seawater, gives the corresponding temperature coefficient for the standard KCl solution, $g_{N,15} = 0.0215°\mathrm{C}^{-1}$.

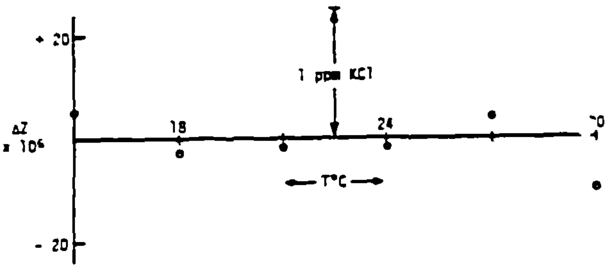

Fig. 3. Deviations of the measured values of $Z_{N,t}$ from (4).

Fig. 4. Deviations of the individual measured values of cell constants R from the averages at 15°C and 24°C for the nine definitive measurements, expressed in units of $1/R$ and equivalent salinity error.

THE VARIABILITY OF STANDARD SEAWATER P79

Because we make simultaneous measurements at two temperatures we are in a position to check for random variations in our bath temperatures or cell constants while standardizations are taking place. Such variations would result in changes in the ratio of the two readings. Consistent variations, which occur in both baths are an indication of variability of the seawater samples themselves—or of our ability to get uncontaminated samples to the inlet of our flow system which is at the end of a fine Teflon tube in the ampoule itself and unlikely to be a source of error. Table IV and Fig. 4 show the deviations from the average values at 15°C and 24°C of the 9 definitive standardizations, which were taken during the period of the 260°C and fused salt runs. It will be seen that the deviations at the two temperatures follow one another almost exactly (σ (difference) = 2.5×10^{-6}, equivalent to $\pm 1 \times 10^{-4}$‰ S!!). Including the "bad" second point the standard deviation from the average at each temperature is 3×10^{-4}‰ S, excluding it $\sigma = 2 \times 10^{-4}$‰ S. Indications are that under normal circumstances any particular lot of standard seawater is reproducible to about $\pm 2 \times 10^{-4}$‰ S, but that the occasional bottle "may" be significantly outside that limit. Because this variation introduces a significant and visible additional noise level into our measurements we follow the practice of using a fixed cell constant (adjusted as necessary for temperature) which is based on the overall average of a number of cell constant determinations over a period of time.

CONCLUSION

Equation (2) makes it feasible to use a relatively broad range of concentrations to establish K_N, or in the future S_{STD} (the salinity of a particular lot of standard seawater using KCl as the conductivity standard, see (2a)), by interpolation or even extrapolation from the measured values to the standard value and making the average deviation zero. It also allows one to calculate the range of effective linearity for a given accuracy of interpolation. However, we suspect that the few workers who carry out KCl-seawater comparisons in future will do their own interpolation of close spaced values to the S_{STD} intercept and (2) will have very limited future usefulness.

Equations (3) and (4), on the other hand, allow one to use a laboratory salinometer at normal temperatures and refer directly to the KCl standard at $Z_{15} = 1$, and may have some future usefulness. The 6–7-percent difference in temperature coefficients between the KCl solution and seawater always requires quite accurate knowledge of the temperature, better than ±0.01°C if one is aiming for an overall accuracy of ±1 ppm S. However, this is still about 20 times better than required for an absolute measurement of the conductivity of standard seawater where Δs(‰) ≈ Δt(°C) from temperature coefficient alone.

The K_N value given here has been averaged with measurements by Poisson [3] and Culkin and Smith [4], also reported in this issue to obtain the value used in the new Practical Salinity Scale [1] which by coincidence is the same as ours. Only the final average value of 32.4356‰ should be used in future determinations of standard seawater salinities.

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Determination of the Concentration of Potassium Chloride Solution Having the Same Electrical Conductivity, at 15°C and Infinite Frequency, as Standard Seawater of Salinity 35.0000‰ (Chlorinity 19.37394‰)

F. CULKIN AND NORMAN D. SMITH

Abstract—**The absolute electrical conductivity at 15 °C of several lots of standard seawater has been measured with great precision as a function of chlorinity. Potassium chloride (KCl) solutions of known concentration and having almost the same conductivity were also measured and the concentration giving the same conductivity at 15°C as 35.0000‰ standard seawater (Chl = 19.37394‰) was found to be 32.4352 g/kg.**

METHOD

IN PRINCIPLE THE method consisted of the following. 1) The absolute electrical conductivity of several batches of standard seawater was measured at 15°C and different frequencies. Each set of measurements was extrapolated to infinite frequency; and, from the resulting relationship between conductivity and chlorinity, the conductivity corresponding to a chlorinity of 19.37394‰ was obtained.

2) In a similar manner, the absolute electrical conductivity, at 15°C and infinite frequency, of a number of KCl solutions of different concentrations was measured. From the resulting relationship between concentration of KCl and conductivity, the concentration corresponding to the conductivity obtained in step 1) was obtained.

PREPARATION OF KCl SOLUTIONS

1) Merck "Suprapur" KCl was first passed through a stainless steel 355-μm sieve. Larger crystals were ground in an agate mortar to pass through the same sieve. A sample of the sieved KCl (*ca* 32.3 g) was then dried in a platinum basin in a muffle furnace. Drying temperatures of >250°C for at least 24 h were found to be satisfactory. After drying the basin and contents were allowed to cool for 12 h in vacuum.

2) The dried KCl was weighed in a stainless steel scoop, fitted with a 3-in long delivery spout, and then transferred to a tared 1-l flask (containing a 1-in Teflon coated magnetic stirrer) by inserting the spout into the neck of the flask and rotating the scoop. The scoop was immediately reweighed to give the weight of KCl taken (w_A).

The weight of KCl, corrected for buoyancy w_V was calculated from

$$w_V = w_A\left[1 + \rho_A\left(\frac{1}{\rho_{\mathrm{KCl}}} - \frac{1}{\rho_W}\right)\right]$$

where

ρ_A density of air, calculated from atmospheric pressure, temperature, and humidity.

ρ_{KCl} density of KCl (solid) = 1.984 g/ml.

ρ_W density of balance weights.

3) An appropriate weight of double distilled water, to give a final concentration in the range 32.42-32.44 gKCl/kg was introduced into the tared 1-l flask containing the KCl. The contents of the flask were then stirred to give complete dissolution of the KCl and finally the flask and its contents were reweighed to give the weight of solution W_S. The weight of solution, corrected for buoyancy W_V was calculated from

$$W_V = W_S\left[1 + \rho_A\left(\frac{1}{\rho_S} - \frac{1}{\rho_W}\right)\right]$$

where

ρ_A density of air

ρ_S density of KCl solution = 1.0171 g/ml for *ca* 32 gKCl/kg at 25°C

ρ_W density of balance weights.

Then KCl concentration = $w_v / W_v \times 1000$ g/kg (in vacuum).

MEASUREMENT OF ELECTRICAL CONDUCTIVITY

The instrument which was used for these measurements was designed at I.O.S. for measuring the absolute electrical conductivity of standard seawater. It comprises a rectangular quartz cell of uniform cross section, open at both ends, which is placed in a silver beaker containing the solution to be measured, with the upper end of the cell above the surface of the liquid. The beaker is contained in an oil-filled bath, servocontrolled at 15° ± 0.005°C, which in turn is surrounded by another bath controlled at 15° ± 0.1°C by means of a mercury contact thermometer. The temperature of the solution is measured by means of a platinum resistance thermometer. The electrode system consists of a shiny platinum gauze, fixed across the bottom end of the cell, and a movable electrode, made from shiny platinum sheet, which travels on a rod passing through the vertical axis of the cell. The movable electrode can be located in two positions, the distance between which is measured by comparison with a quartz standard length by means

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The authors are with the Institute of Oceanographic Sciences, Wormley, Godalming, Surrey, England.

of a Michaelson interferometer. The whole system is sealed to prevent evaporation during measurements.

The beaker containing the cell was filled with the solution (*ca* 1 kg) which was stirred to achieve temperature equilibrium at 15° ± 0.0001°C and, with the movable electrode in the upper position, the ac bridge was balanced. The electrode was then moved the fixed distance to the lower position and the change in resistance was compared with a standard resistance to 0.0001 percent. From the resistance thus measured, the cross sectional area, and the distance through which the electrode was moved, the conductivity of the solution was obtained. Measurements were made at 1.5, 3.0, 4.5, 6.0, 9.0, and 10.0 kHz and the results were extrapolated to infinite frequency.

RESULTS

Standard Seawater

Batch No.	Chlorinity (‰)	Conductivity (mmho·cm^{-1}) at 15°C and Infinite Frequency
P59	19.3770	42.9202
P60	19.3765	42.9193
P68	19.3718	42.9095
P71	19.3740	42.9139
P72	19.3748	42.9163
P75	19.3740	42.9146
P77	19.3755	42.9168
P79	19.3760	42.9178
P80	19.3782	42.9219
P82	19.3706	42.9075
P84	19.3762	42.9181

Linear regression, conductivity = 5.325053 + 1.940181 Cl‰. For chlorinity 19.37394‰, conductivity = 42.9140 mmho·cm^{-1}.

KCl Solutions

KCl Concentration (gKCl/kg)	R_{15} (at Infinite Frequency)
32.42894	0.999802
32.43328	0.999937
32.43980	1.000146
32.42909	0.999792
32.43362	0.999955
32.43048	0.999865
32.43304	0.999951
32.43661	1.000051
32.43303	0.999930
32.43684	1.000051
32.43040	0.999844
32.43232	0.999902
32.43552	0.999983
32.43357	0.999944
32.43283	0.999927
32.43072	0.999853
32.42777	0.999776

$$R_{15} = \frac{\text{Conductivity of KCl solution at 15°C and infinite frequency}}{\text{Conductivity of standard seawater of chlorinity 19.37394‰ (at 15°C and infinite frequency).}}$$

Linear regression equation: KCl concentration = 0.82066 + 31.61455R_{15}. Hence for R_{15} = 1.0, KCl concentration = 32.43522 g/kg.

CONCLUSION

A KCl solution containing 32.4352 gKCl/kg has the same electrical conductivity, at 15°C and infinite frequency, as standard seawater of salinity 35.0000‰ (chlorinity 19.37394‰).

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The Concentration of the KCl Solution Whose Conductivity is that of Standard Seawater ($35^{o}/_{oo}$)at 15°C

ALAIN POISSON

***Abstract*—The concentration of the potassium chloride solution (KCl) which has the same conductivity as 15°C at P79 standard seawater corrected to $35.0000^{o}/_{oo}$ has been evaluated. The variation of the conductivity ratio of KCl solutions to standard seawater ($35^{o}/_{oo}$) has been measured between 14.8 and 15.2°C for KCl solutions whose concentration varies from 32 to 33 $g \cdot kg^{-1}$.**

INTRODUCTION

FOR SEVERAL YEARS, we have been studying—as a member of the Joint Panel—the problem of the definition of salinity and standardization of standard seawater in electrical conductivity; for this purpose, it has been proposed several times to use a solution of KCl [1]-[4].

The solution recently proposed by the Joint Panel on Oceanographic Tables of Standards (JPOTS), explained in detail elsewhere is close to the solution that we had proposed: on one hand, standard seawater will now be standardized in electrical conductivity at 15°C relatively to a KCl solution and, on the other hand, salinity will also be defined relatively to this KCl solution. Thus the aim of this work was to measure the concentration of the KCl solution which, at 15°C has the same electrical conductivity as standard seawater with a $35^{o}/_{oo}$ salinity. We describe here the method we have used to determine this concentration and the results we have obtained. This work has also been performed independently in two other laboratories with different methods [7], [8].

The measurement technique and the intermediate calculations, briefly presented here are given in more detail in a UNESCO technical paper [9].

APPARATUS

The method we have used consists of measuring the resistance R and the temperature t of a definite volume of a KCl solution or of standard seawater. The specific conductance of the KCl solution is determined by

$$\chi(\mathrm{KCl}) = a/R(\mathrm{KCl}) \tag{1}$$

where a is the cell constant at the temperature of the measurement and R(KCl) the measured resistance of the KCl solution.

In the same way, for standard seawater

$$\chi(sw) = a/R(sw). \tag{2}$$

Since these measurements are performed in the same cell, and in the same conditions, the cell constant remains the same for the two sets of measurements. To have

$$\chi(\mathrm{KCl}) = \chi(sw)$$

it is sufficient to determine that

$$R(\mathrm{KCl}) = R(sw). \tag{3}$$

The results of these measurements are presented in resistance units (Ω), as obtained directly from the experiment. Resistance was measured with a Jones-type bridge (Leeds and Northrup, type 4666), temperature with a thermometric bridge (ASL, type H7) and a platinum thermometer (Tinsley, type 5187 SA), and the volume of the solution was defined by a Jones-type cell (Beckman, type 6J) with a cell constant equivalent to 120 cm^{-1}. The temperature was measured with an accuracy of $\pm 1.10^{-3}$°C and a precision of 0.2×10^{-3}°C. The resistance given in the tables is the pure ohmic resistance of the solution. In particular, the influence of the frequency w of the current through the solution was eliminated by extrapolating $\Delta R_w \propto 1/w$ to infinite frequency. A previous study had shown that at high frequencies (8000, 10 000 Hz), the Falkenhagen effect is not negligible. The measurements which were used for the extrapolation were therefore performed at 2000, 2500, 3000, and 4000 Hz. The temperature corrections of the Jones-type bridge, the elimination of the resistances of the connecting wires, and the extrapolation to infinite frequency were performed for each measurement.

METHOD

We first measured the resistance of a number of ampoules of standard seawater from lot P79. That lot was chosen because it is on the basic line $\chi(sw) = f(\mathrm{Cl}^{o}/_{oo})$ of the latest batches of standard seawater prepared at Wormley (Culkin, private communication). We then measured the resistances of a number of KCl solution, close to the resistance of standard seawater found above and of known concentrations as calculated from the weight of KCl and of the distilled water used to prepare them.

DETERMINATION OF THE CELL RESISTANCE FOR SEAWATER OF EXACTLY $35^{o}/_{oo}$S AND 15°C

Since the measurements were not made at exactly 15°C and $35^{o}/_{oo}$S, we first determined by measurements presented elsewhere [10], the coefficients $\Delta R(sw)/\Delta t$ and $\Delta R(sw)/\Delta S$ close to the resistance of standard seawater at 15°C. The re-

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The author is with Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, Tour 24, 4, Place Jussieu, 75230 Paris Cedex 05, France.

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TABLE I
RESISTANCE OF STANDARD SEAWATER P79 CORRECTED AT 15°C AND 35‰

Ampoule Number	Corrected Resistance (Ω)
1-1	2789.836
1-2	2789.832
2	2789.882
3	2789.888
4	2789.794
5	2789.884
6	2789.864
7	2789.828
8	2789.898
9	2789.870
10	2789.817
11	2789.861

sistances of the batch P79 samples, corrected to 15°C and 35‰S are given in Table I. To convert the 19.3760‰ chlorinity indicated on the ampoule into salinity, we used the recommended formula [5].

$S = 1.80655\ Cl.$

Therefore, salinity adopted for standard seawater P79 was 35.0037‰.

The mean value of the resistance of standard seawater P79 at 15.0000°C, corrected to 35.0000‰S was 2789.855 Ω ± 0.032 Ω.

DETERMINATION OF THE CONCENTRATION OF THE KCl SOLUTION HAVING A RESISTANCE OF 2789.855 Ω AT 15°C

Preparation of the KCl Solutions

All solutions whose concentration must be known with great accuracy were prepared with water double distilled on quartz by accelerated evaporation and with Merck "Suprapur" KCl.

The distilled water was set in equilibrium with the air of the laboratory before preparing the solutions. In a previous study, the KCl used had been purified by recrystallizing it three times, oven-dried at about 100°C, then fused in a platinium crucible. This study has shown that Merck "Suprapur" KCl has sufficient purity for the work carried out here. The data are thus relative to solutions directly prepared with Merck "Suprapur" KCl, without additional purification. One set was prepared with KCl oven-dried at 150°C in vacuum, and a second set with fused KCl.

For all solutions, corrections were made for evaporation in the flask where the KCl solution was prepared, and for air buoyancy on KCl and on the solution. The weights in vacuum (M_{vac}) were calculated with the equation

$$M_{vac} = m(1 + 11.8 \times 10^{-6}) \frac{1 - (a_{tph}/7.76)}{1 - (a_{tph}/\rho)} \qquad (4)$$

where a_{tph} is the density of air at the time of weighing, at temperature t, pressure p, and humidity h. ρ is the density of the body to be weighed and m the value read on the Mettler balance. For those calculations we used

ρ KCl (solid) = 1.984 g·cm³

ρ platinium = 21.45 g·cm³

ρ distilled water = ρ S.M.O.W

The density of KCl solutions is given in the *Handbook of Chemistry* (46th edition). Corrected to the temperature of the weighings (23°C), it can be written as

$$\rho \text{ (solution KCl)} = (0.9976 + 6.43 \times 10^{-4}\ C)\ \text{g·cm}^3$$

where C is the concentration in g(KCl)/kg of solution.

The fused KCl was weighed with a Mettler balance type M5GD (20 g max to 1 μg) in a platinum crucible of precisely known mass; the crucible was then transferred into a 1-l screw plugged flask and the total weight determined on a Mettler balance type B5C 1000 (1000 g max to 0.2 mg). When introducing the distilled water, only a small amount of fused KCl dissolves. Therefore, a correction was made for the air displaced by the added distilled water.

The solutions obtained from dried KCl were prepared in the same way. In this case, however, KCl is in the form of smaller crystals rather than lumps, and thus while introducing distilled water, all of the KCl dissolves. Therefore, the correction was made for the air displaced by a corresponding quantity of KCl solution.

The Variation of the Resistance of KCl Solutions Around 15°C and 32.43 g·kg⁻¹

A previous study had enabled us to determine that a solution of approximately 32.44 g of KCl/kg of solution has the same electrical conductance as standard seawater with a 35‰ salinity at 15°C. Therefore, we first measured the variations of resistance of KCl solutions around 32.44 g·kg^{-1} and 15°C as a function of temperature and concentration.

Measurement of ΔR(KCl)/Δt: These measurements were carried out using a KCl solution with a concentration close to 32.44 g·kg^{-1} prepared from distilled water and KCl dried for about 4 h at 150°C. The ratio ΔR(KCl)/Δt has been estimated at −61.0 Ω·°C^{-1}.

This ratio does not need to be known with a great accuracy, for the measurements of resistance of the KCl solutions to be corrected (Tables II and III) were all carried out at temperatures very close to 15°C. Therefore, the necessary corrections will be small.

Measurement of $\Delta C/\Delta R$(KCl): We made three sets of dilutions, each from strong concentrations of about 200 g·kg^{-1}, prepared without special precautions. The corrections for evaporation were made for the secondary dilutions.

Each set of data $C = f(R(\text{KCl}))$ was fitted under the form of a polynomial

$$C = A_0 + A_1 R^{1/2} + A_2 R + A_3 R^{3/2} \qquad (5)$$

TABLE II
RESISTANCE OF "DRIED KCl SOLUTION" AT 15°C AND THEIR CONCENTRATION CORRESPONDING TO THE RESISTANCE OF STANDARD SEAWATER OF 35 ‰ AT 15°C*

Solution Number	Merck Flask	Time of Drying	Resistance Measured Corrected at $t = 15°C$	Concentration Measured (g/kg)	Concentration* Corrected for $R = 2789\ 855\ \Omega$ (g/kg)
1	B	24 h	2793.265	32.4071	32.4482
2	B	24 h	2791.058	32.4225	32.4370
3	A	4 days	2790.937	32.4232	32.4362
4	A	4 days	2789.368	32.4416	32.4357
5	A	4 days	2789.946	32.4349	32.4360
6	A	4 days	2789.065	32.4447	32.4352

* $\bar{C} = 32.4360$, $\sigma = 6.7 \times 10^{-4}$.

TABLE III
RESISTANCE OF "FUSED KCl SOLUTIONS" AT 15°C AND THEIR CONCENTRATION CORRESPONDING TO THE RESISTANCE OF STANDARD SEAWATER OF 35‰ AT 15°C

Solution Number	Merck Flask	Measured Resistance Corrected at 15°C (Ω)	Concentration Measured (g/kg)	Concentration* Corrected for $R = 2789.855\ \Omega$ (g/kg)
1	B	2791.255	32.4195	32.4364
2	B	2791.800	32.4130	32.4365
3	B	2790.674	32.4261	32.4360
		2790.708	32.4261	32.4364
4	B	2790.486	32.4280	32.4356
		2790.502	32.4280	32.4358
5	C	2789.714	32.4372	32.4355
		2789.713	32.4372	32.4355
6	C	2789.358	32.4410	32.4350
		2789.380	32.4410	32.4353
7	C	2789.956	32.4345	32.4357
		2789.940	32.4345	32.4355
8	C	2789.565	32.4386	32.4351
		2789.601	32.4386	32.4355

* $\bar{C} = 32.4357$, $\sigma = 4.7 \times 10^{-4}$.

where $R = R(\text{KCl})$. The three polynomials obtained were then normalized to $R = 2789.80\ \Omega$ for $C = 32.436\ \text{g}\cdot\text{kg}^{-1}$.

Finally, the experimental data, normalized to this point have been fitted to a polynomial of the same form as (5) above whose coefficients are

$$A_0 = 521.2965$$

$$A_1 = -26.6371$$

$$A_2 = 0.570524$$

$$A_3 = -5.772865 \times 10^{-3}$$

$$A_4 = 2.27518 \times 10^{-5}.$$

From (5) we obtain

$$\frac{dC}{dR} = \frac{A_1}{2\sqrt{R}} + A_2 + \frac{3}{2} A_3 \sqrt{R} + 2A_4 R. \tag{6}$$

Since the resistance of standard seawater at 15°C is 2789.855 Ω, the slope at 15°C is given by

$$\Delta C/\Delta R(\text{KCl}) = -12.06 \times 10^{-3}\ \text{g} \cdot \text{kg}^{-1} \cdot \Omega^{-1}.$$

We have used this ratio to correct the experimental data on the KCl solution concentrations given in the following section. The procedure is justified because again these corrections are very small.

Determination of the Concentration of the KCl Solution Having a Resistance of 2789.855 Ω at 15°C

Solutions of Dried KCl: The KCl solutions were prepared from KCl dried in an oven in vacuum at 150°C for 24 h (sol 1) or for 4 days (sol 2, 3, 4, 5). The KCl used came from three different flasks (A, B, C) directly delivered by the manufacturer. The resistances measured and the concentrations calculated from the weights of KCl and distilled water are given in Table II. In the calculation of the average concentration $\bar{C}$ and of the standard deviation σ, solution 1 which was obviously erratic was not taken into account.

Solutions of Fused KCl: The solutions were prepared from KCl fused in an oven at about 850°C. The data given in Table III; the average concentration $\bar{C} = 32.4357\ \text{g}\cdot\text{kg}^{-1}$ is slightly lower than the concentration obtained with dried KCl ($\bar{C} = 32.4360\ \text{g}\cdot\text{kg}^{-1}$), but the two average concentrations remain within their respective experimental errors. We can suppose that KCl had not been sufficiently dried, and that there was some water left in the salt crystals, which would account for the slight difference between the two sets of data. The average value of all the data (13 independent solutions) is $\bar{C} = 32.4358\ \text{g}\cdot\text{kg}^{-1}$ with a standard deviation of $5 \times 10^{-4}\ \text{g}\cdot\text{kg}^{-1}$

THE CONTRIBUTION OF THE SPECIFIC CONDUCTANCE OF DISTILLED WATER TO THE CONDUCTANCE OF THE 32.4358-g·kg⁻¹ KCl SOLUTION

The specific conductance of the KCl solution $\chi(\text{KCl})$ is the sum of the specific conductance of K^+ and Cl^- ions of KCl, $\chi(\text{K}^+\text{Cl}^-)$, and the specific conductance of the distilled water $\chi(w)$ used to prepare it:

$$\chi(\text{KCl}) = \chi(\text{K}^+\text{Cl}^-) + \chi(w). \tag{7}$$

Now the conductance of our distilled water can vary from $0.5 \times 10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}$ for a water nearly free of gas to $2 \times 10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}$ and even more for a distilled water set in equilibrium with air by bubbling. The distilled water we used had previously been set in equilibrium with the air of the laboratory without bubbling. Its conductance was measured with the method of Justice (private communication):

$$\chi(w) = 1.0 \times 10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}.$$

Hence, from (1), (2), and (7)

$$R(\text{K}^+\text{Cl}^-) = \frac{aR(\text{KCl})}{a - 1.0 \times 10^{-6} R(\text{KCl})} \tag{8}$$

where $a \cong 120\ \text{cm}^{-1}$ and $R(\text{KCl}) = 2789.855\ \Omega$. Consequently $R(\text{K}^+\text{Cl}^-) = 2789.920\ \Omega$ and the conductance of pure water therefore is equivalent to a resistance of $-0.065\ \Omega$, that is to say is equivalent to (from the coefficient $\Delta C/\Delta R$ (KCl) previously determined) $+\ 0.0008\ \text{g}\cdot\text{kg}^{-1}$ in concentration of the KCl solution.

R_{KCl} AS A FUNCTION OF C AND t NEAR 35‰ S AND 15°C

The variation of the ratio $R_{\text{KCl}} = \chi(\text{KCl})_{C,15,0}/\chi(sw)_{35,15,0}$ around 15°C and $32.4\ \text{g}\cdot\text{kg}^{-1}$ is needed over an adequate area of temperature and concentration for the standardization of future standard seawater which will be made at temperatures and concentrations slightly different from 15°C and $32.4358\ \text{g}\cdot\text{kg}^{-1}$.

This ratio can be written

$$R_{\text{KCl}} = 1 + A_1(C - 32.4358) + A_2(C - 32.4358)^2 + A_t(t - 15) \tag{9}$$

where A_1 and A_2 are constants calculated later

$$A_t = \frac{d}{dt}\, \frac{\chi(\text{KCl})_{32.4358,15,0}}{\chi(sw)_{35,t,0}} \text{ at } 15°\text{C}. \tag{10}$$

A_t had been measured before:

$$A_t = -0.00107°\text{C}^{-1}.$$

With polynomial (5) normalized at $R = 2789.855\ \Omega$ for $C = 32.4358\ \text{g}\cdot\text{kg}^{-1}$ and the resistance of standard seawater at 15°C (2789.855 Ω), the ratio R_{KCl} was measured at various concentrations of the KCl solution.[1] These data were fitted in a polynomial of the second degree in concentration C, normalized at $R_{\text{KCl}} = 1$ for $C = 32.4358\ \text{g}\cdot\text{kg}^{-1}$:

$$R_{\text{KCl}} = 1 + 2.9722 \times 10^{-2}(C - 32.4358) - 8.1 \times 10^{-6}(C - 32.4358)^2. \tag{11}$$

The variation of R_{KCl} around the point of equivalence is then

$$R_{\text{KCl}} = 1 + 2.9722.10^{-2}(C - 32.4358) - 8.1 \times 10^{-6}(C - 32.4358)^2 - 1.07 \times 10^{-3}(t - 15). \tag{12}$$

This equation can be used for temperatures from 14.8°C to 15.2°C and for KCl solutions with concentrations between $32\ \text{g}\cdot\text{kg}^{-1}$ and $33\ \text{g}\cdot\text{kg}^{-1}$.

CONCLUSION

In summary, the specific conductance at 15.0000°C of standard seawater P79 corrected to 35.0000‰ S is identical to that of a solution of 32.4358 gKCl/kg of solution (in vacuum) whose specific conductance of pure water is $1.0 \times 10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}$. R_{KCl} near the point of equivalence varies according to (12) above.

The value of KCl concentration found in our laboratory has been used with those given by Dauphinee *et al.* [7] and Culkin *et al.* [8] to calculate the standard concentration used in the "Practical Salinity Scale 1978" [6] by JPOTS.

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[1] Note that $R(\text{KCl})$ is the *resistance* of the solution; R_{KCl} is the resistance *ratio* to the standard value.

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MEASUREMENT OF THE CONDUCTIVITY RATIO

AS A FUNCTION OF SALINITY, TEMPERATURE AND PRESSURE

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The Electrical Conductivity of Weight Diluted and Concentrated Standard Seawater as a Function of Salinity and Temperature

THOMAS M. DAUPHINEE, SENIOR MEMBER, IEEE, JOHN ANCSIN, H. PETER KLEIN, AND M. JOHN PHILLIPS

Abstract—The ratios $R_{s,t,o}$ of electrical conductivity of seawater samples of precisely known salinity to standard seawater at the same temperature have been measured over a wide range of salinities from 0 to $42^{\circ}/_{oo}$S and over the full range of oceanic temperatures from −2 to 35°C.

The samples with $S < 35^{\circ}/_{oo}$ were prepared by accurate weight dilution of standard seawater with distilled water. High salinity samples were prepared by fast evaporation of standard seawater and subsequent weight dilution into the already determined $< 35^{\circ}/_{oo}$ range.

An equation was derived which expresses the S versus $R_{s,t,o}$ relationship very precisely from $1\text{–}42^{\circ}/_{oo}$ and at all temperatures, i.e.,

$$S = f_1(R_{s,t,o}) + f_2(R_{s,t,o}, t)$$

$$= \sum_{n=0}^{5} a_n R^{n/2} + \frac{\Delta t}{1 + k\Delta t} \sum_{n=0}^{5} b_n R^{n/2}$$

where $\Delta t = t - 15^{\circ}\mathrm{C}$, $R = R_{s,t,o}$; only the first term f_1 is required at 15°C.

The effect of temperature on the electrical conductivity of standard seawater was also measured. The ratio r_t of the conductivity at temperature t to the conductivity at 15°C ($C_{35,t,o}/C_{35,15,o}$) is very accurately expressed by a fourth degree equation in t,. i.e,

$$r_t = \sum_{n=0}^{4} c_n t^n.$$

These two equations are sufficient for all salinity determinations at normal atmospheric pressure.

INTRODUCTION

IN CONNECTION with our work on *in-situ* measurements of conductivity, temperature, and pressure in the ocean we have found it necessary to develop facilities for laboratory calibrations and testing of the equipment. This led to the development of a new and very precise continuous flow system for comparing the conductivity of samples of seawater with standard seawater at the same temperature, for use in salinity determinations. This in turn ultimately led to production of the Guildline "Autosal" laboratory salinometer which is now in use in almost every major oceanographic standardizing laboratory in the world.

We then adapted the basic concept of the salinometer system to allow simultaneous measurements on the same sample at two different temperatures and began a comprehensive study of the effect of temperature and salt concentration on the conductivity of seawater samples made from weight diluted or concentrated samples of standard seawater. The measurements were made from below the freezing point to 35°C and from $42^{\circ}/_{oo}$ S to $1^{\circ}/_{oo}$ S with some measurements at 15°C carried down to a few ppm S to determine the shape of the conductivity versus salinity curve at very low salinities. In addition, we carried out determinations of the concentration of potassium chloride (K) giving a conductivity ratio R_K of 1 to standard seawater at 15°C, and of the effect of both a few ppt variations around the standard value and temperature between 15° and 30°C which are reported elsewhere in this issue [1].

The conductivity measurements were undertaken as part of an international program sponsored by UNESCO-SCOR-IAPSO-ICES (Joint Panel of Experts on Oceanographic Tables and Standards)[2]. The program includes a redefinition of salinity and development of a standard set of equations and tables for calculation of the salinity of seawaters both in the laboratory and in the ocean. These will be recommended for use by all oceanographers after approval by the various sponsoring bodies. The work reported here forms a substantial part of the basis for the new equations

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The authors are with the National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6.

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and in fact led to the form of the surface pressure equations that have been used. Similar measurements using entirely different equipment were carried out by A. Poisson (Paris, France) [3] and confirmatory work on the effect of temperature on the conductivity at various salinities was carried out, using a third type of apparatus, by Bradshaw and Schleicher (Woods Hole, U.S.A.) [4], who have also repeated with greater accuracy their earlier study [4a] of the effect of pressure on the conductivity. In addition, Culkin and Smith (Wormley, U.K.) [5] and Poisson [6] also carried out determinations of the KCl equivalent of standard seawater at 15°C.

It is extremely gratifying to report that, with few exceptions, wherever comparisons are possible, agreement between the different laboratories using entirely different equipment has been better than the equivalent of ±1 ppm S, almost an order of magnitude better than has been the norm. Except for the effect of temperature near and below 0°C and at salinities below 2‰ the new work is not seriously different from equations fitted to the earlier work of Brown and Allentoft [7] on which many oceanographic calculations have been based.

Because of this solid data base the new equations should be accepted with great confidence by the oceangraphic community. It should be pointed out that the equations given in this paper represent the best fit to our work *only* and *are not* recommended for adoption by anyone. Although the differences from the new scale are negligible the averaging in of other data has resulted in different constants for the equations of the official version and only the official constants should be considered in the interests of completely consistent reporting of oceanographic data.

Practical salinity determinations at zero (surface) pressure are always made by taking the ratio (R, W) of conductance C of the sample to the conductance of the same cell with standard seawater (35‰) either at the same temperature (R_t) or at some standard reference temperature, usually 15°C.

$R_t = C_{s,t,o}/C_{35,t,o}$, for most lab measurements

$W_t = C_{s,t,o}/C_{35,15,o}$, for most field measurements.

The above quantities[1] are related by the function

$$r_t = C_{35,t,o}/C_{35,15,o} = f_r(t) \tag{1}$$

which expresses the effect of temperature on the conductivity of standard seawater, i.e.,

$$W_t = R_t r_t. \tag{2}$$

In-situ measurements of W also include the effect of pressure and this may be expressed for calculation purposes as

$$W_p = W_t(1 + \alpha). \tag{3}$$

The basic equation for the calculation of salinity, whatever its form may be, is that for the standard temperature of 15°C at zero pressure

$$S = f_1(R_{15}). \tag{4}$$

Measurements at other than the standard conditions are then usually treated as perturbations of the basic equation. For instance, if the measuring and the reference temperatures are the same but *not* 15°C and $P = 0$ substitution of R_t in f_1 alone creates a small error and a correction function f_2 is required, i.e.,

$$S = f_1(R_t) + f_2(R_t, t).^2 \tag{5}$$

If the reference is at 15°C and $P = 0$ one can substitute from (2)

$$R_t = W_t/r_t.$$

For measurements *in situ* one substitutes, combining (2) and (3)

$$R_t = W_p/(1 + \alpha) \cdot r_t$$

instead.

One possible form of the general expression for S is therefore

$$S = f_1(W_p/(1 + \alpha) \cdot r_t) + f_2(W_p/(1 + \alpha) \cdot r_t, t) \tag{6}$$

from which terms may be dropped as appropriate to simplify the calculations.

The present measurements along with those of other workers were undertaken with a view to determining the best form and appropriate constants for the expressions for r_t and S.

APPARATUS

The measuring system we have used, illustrated in Figs. 1-4, is essentially the same as that used by Dauphinee and Klein [8] in their measurement of the temperature coefficients of standard, synthetic, and Atlantic waters near 35‰S. The sample water (Fig. 1) is driven by air pressure from an aquarium pump from a sample bottle via a thin Teflon tube. This tube divides to direct the water into two fine bore stainless steel heat exchangers (2.5 m long, 1 mm I.D.) which are mounted in different temperature controlled baths. From each coil the water passes to one of the two conductance cells, also in the bath, and from the cell, through an insulated exit tube to the side of the bath where it falls in droplets into a funnel leading to the waste bottle. A pinch clamp on one input line allows balancing of the flows between the cells as the water viscosity changes with change of temperature.

The cells have four sidearms projecting upwards and each containing a helical Pt10Rh platinized electrode and a Teflon

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[1] Subscripts s, t, and o, refer to salinity, temperature, and pressure (o = 1 atmos), respectively, of the sample under consideration, one or other subscript may be omitted when the meaning is obvious.

[2] Previously the correction has been made to $R_{s,t,o}$ to bring it to $R_{s,15,o}$. The reason for the change is discussed later.

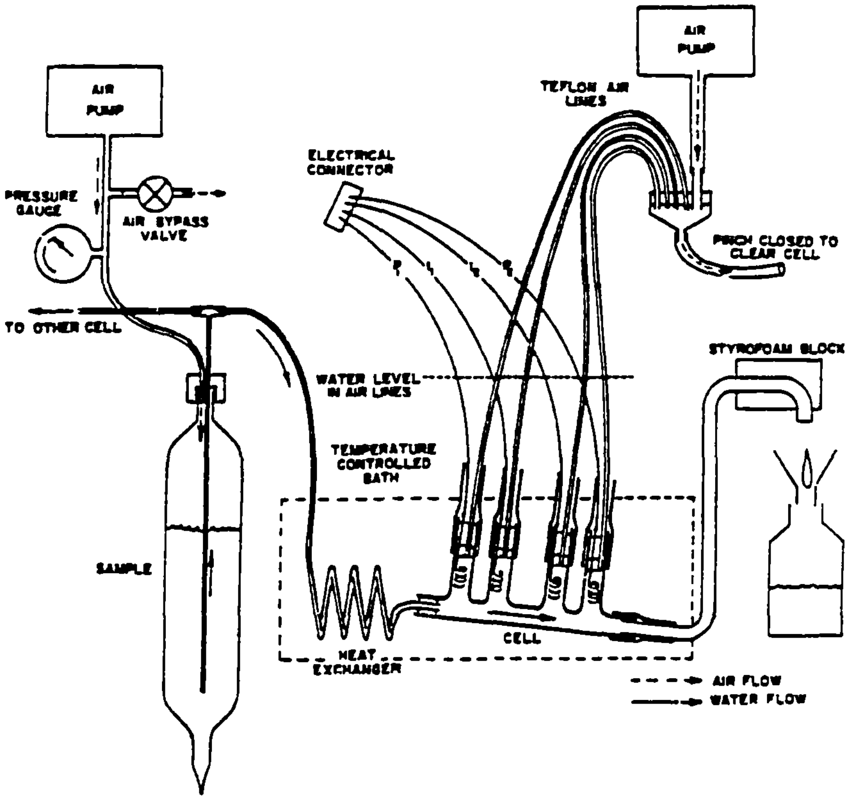


Fig. 1. The flow system for sample water.

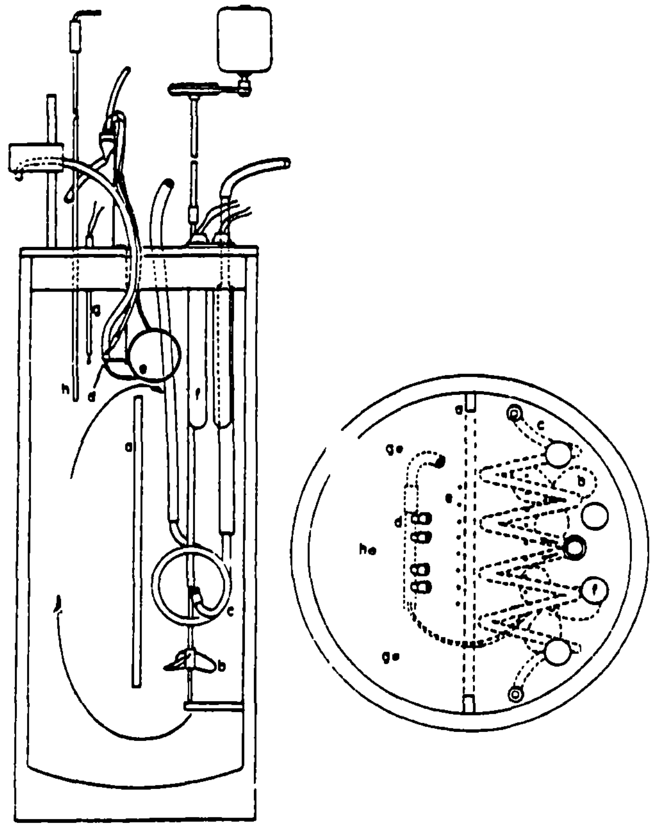
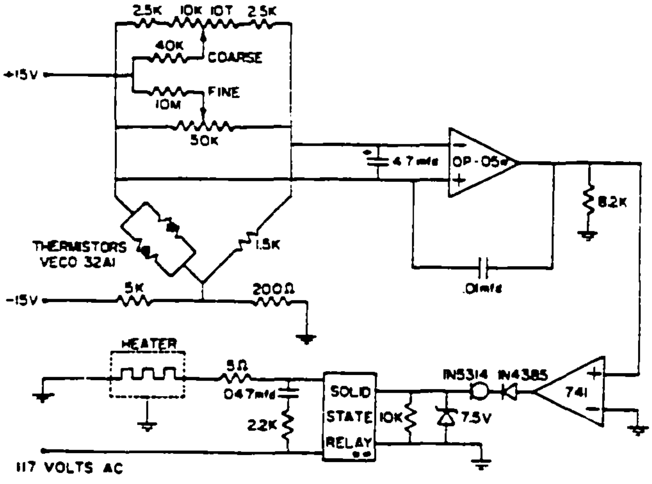


Fig. 2. The component layout in the bath. (a) Up–down flow separator. (b) Propellors. (c) Cooling coil. (d) Conductivity cell. (e) Heat exchanger. (f) Heater lamps. (g) Control thermistors. (h) Resistance thermometer.



* PRECISION MONOLITHICS MONO OP-05
** TEXAS INSTRUMENTS TIH502

Fig. 3. The bath temperature-control circuit. Thermistors are Veco, 32A1, 2 kΩ at 25°C partly blackened on one side; 1N5314 - 5-mA current regulation diode; heaters are 4–20-W incandescent bulbs.

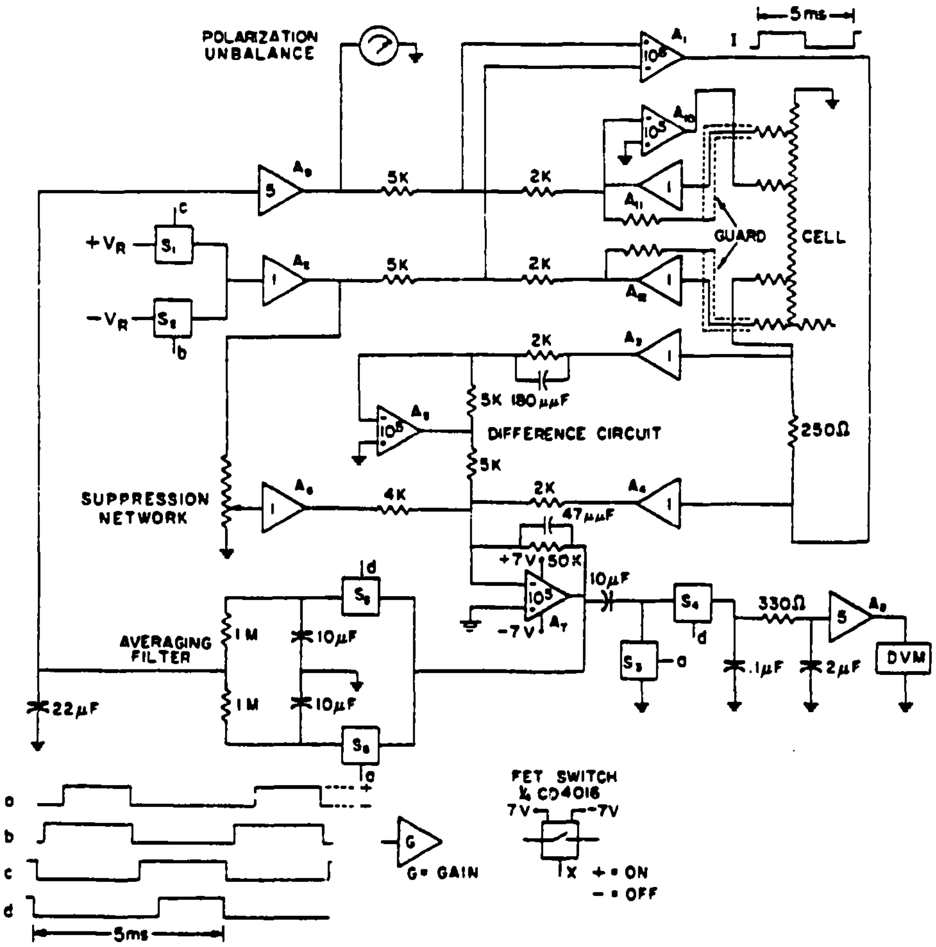


Fig. 4. The conductance measuring circuit. S_1 -- S_6 are C/MOSFET switches (RCA type 4016); amplifiers are AD741 except A_{11}, A_{12} (FET input BB3522 and the current driver (MONO-OP 05).

air escape tube which allows complete filling of the sidearms and flushing of the cell by forcing air down them. To ensure that as much water as possible is driven from the cell on flushing, the cell is mounted at an angle with the exit end the lowest part of the system. This has the added advantage that any bubbles that might be formed at higher temperatures in the heat exchanger are trapped at the inlet end of the cell before they get to the measuring zone. The air escape tubes are electrically isolated in a common header by projecting them vertically downward in a square array about the continuous air flow from a second aquarium pump which keeps them dry. Flushing is accomplished by pinching of the header outlet tube. Leakage to the exit end of the cell at low measuring temperatures is prevented by passing the exit tubes through a grease seal in a styrofoam block whose outer surface stays above the condensation temperature. Isolation from the waste system results from the separation of the output droplets.

The bath temperatures are read with a Rosemount platinum resistance thermometer and a Guildline "Dauphinee" direct reading bridge [9] with interpolation by deflection to 0.2 m°C.

The baths (Fig. 2) are of 40- and 60-l capacity and stir with a cycle time of a few seconds. They are cooled via copper coil *c* by cold nitrogen gas evaporated from the liquid by a Variac controlled heater. Actual temperature control is by tubular incandescent lamp heaters *f* powered in on-off mode by a thermistor controlled supply. The control circuit, shown in Fig. 3, utilizes two thermistors in parallel (or singly for checking purposes), with some of the light energy fed directly to them so that internal heating shortens the cycle time to about 1/2 s. Experience has shown that this simple circuit routinely controls the bath temperatures to within ±0.2 m°C for many hours and since this is better than the reproducibility of the copper thermometer system previously used, the thermometers were dispensed with in favor of frequent direct reference to the platinum scale.

The conductance measuring circuit is shown in Fig. 4. The cell operates on square wave ac current generated in the cell by solid-state switching (S_1, S_2, A_2) of a precisely regulated $\pm 1/10^5$ reference voltage $\pm V_R$. The current is controlled (A_1, A_{11}, A_{12}) to keep the square wave component of voltage across the cell potential leads constant, so that the current is proportional to the effective conductance of the cell between the potential electrodes. This current is measured by reading the voltage difference across a 250-Ω (or 200-Ω at high conductances) resistor in series with the cell with an isolating differential amplifier (A_3, A_4, A_5). The summing point is held at zero potential by an inverting difference amplifier A_7 plus a suppression signal (A_6) adjustable in 22 steps which is derived from the reference square wave. The output of the difference amplifier is demodulated (S_3, S_4) to dc with a blocking capacitor in series to eliminate zero offset, and after further dc amplification (A_8) to exactly 5-V/suppression step is read with a precision DVM. Ratios have been chosen so that a cell resistance exactly equal to the series reference resistor represents exactly 20 steps of the suppression dial, which is read as 100 and added algebraically to the DVM reading to obtain the conductance in arbitrary units. Our cells give a reading of about 85 with standard seawater at 15°C.

A simple four-pole selector switch and plug connections can be used to select and interchange the cells since the circuit is effectively independent of lead resistances and thermal emf's. The effect of interlead capacitance which could cause oscillations is eliminated by use of tape wiring with the conductors on either side of the potential leads driven at the same potential (guard). Current offset due to polarization is eliminated to sufficient approximation by a switched (S_5, S_6) averaging filter which automatically adjusts the bias of the drive circuit (A_9) to keep the dc component of cell current small. Shunt current to the heat exchanger is eliminated by holding the potential lead at that end at zero potential (A_{10}). We use the inner cell electrodes as current leads because this reduces the driving voltage required of A_1. The extremely low input current of FET amplifiers A_{11}, A_{12} and regulation of the current to the proper value prevent errors due to changes of potential and current electrode polarization or resistance during the course of one cycle. Balances are normally reproducible from flush to flush to a few parts in 10^6, equivalent to about ±0.1 ppm S.

PREPARATION OF SOLUTIONS

The salinity of a solution is defined as

$$S = \frac{x}{x+y} \tag{7}$$

where S, x, and y are the salinity, mass of salt, and mass of pure water, respectively.

In order to determine these masses it is necessary to make appropriate corrections for air buoyancy using the relations

$$M_o - m_o = M_w - m_w$$

where M_o, M_w are the true masses of the object and the weights of the balance and m_o and m_w are the masses of air displaced by object and weights, respectively. We can also write

$$M_o - \rho_a V_o = M_w - \rho_a V_w$$

where ρ_a is the density of air, corrected for barometric pressure, temperature, and humidity, and V_o and V_w are the volumes, of object and weights. Finally

$$M_o = M_w \left(1 - \frac{\rho_a}{\rho_w}\right) + \rho_a V_o. \tag{8}$$

The samples for conductivity measurements were prepared in glass ampoules of about 285-cm^3 volume made by rounding off one end of a standard seawater bottle and cutting and flame polishing the narrow filling tube at the other end. Each bottle had its own cap made of a short (1-cm) piece of rubber tube with a Plexiglas disk across one end. The caps typically weighed about 0.7 g. The true mass of each ampoule was determined using (8) taking the density of glass to be 2.21 g/cm^3, and, in subsequent mass determinations of solutions in the bottles, the bottle mass was corrected for the prevailing air conditions. The true mass of the bottles was effectively invariant over the several month duration of the experiments. However, the caps increased in mass slightly by up to 1 or 2 mg/wk and their masses were determined quite frequently.

Four kinds of solutions were prepared:

1) Dilute solutions (<35‰ S) of precisely known salinity made from standard seawater and very pure distilled water.

2) concentrated solutions (>35‰ S) made from standard seawater concentrated by evaporation and diluted if necessary to an approximately known salinity.

3) dilute solutions (28 to 35‰ S) made by dilution of type 2 concentrated solutions *after* part of the water had been used for a precise conductivity measurement,

4) solutions of pure KCl having concentrations around 32.435 g/kgKCl and giving a conductivity ratio to standard seawater at 15°C close to unity. These solutions are discussed in another paper [1] in this issue.

To prepare the type 1 dilute solutions the mass of distilled water required to give the desired salinity when standard seawater was added to give a total volume of 200 to 220 cm^3 was first calculated. This amount of distilled water was then introduced by using air pressure to drive the water from its container (≈550 ml^3) through a thin Teflon tube into the ampoule. After making sure that the air had been saturated with water vapour the true mass of distilled water was determined from total mass less the bottle and cap masses with appropriate corrections according to (8) using the expression $V = m(1 + \rho_a)/\rho_w$ for the water volume (m being the water mass and ρ_w its density). The assumption was made that all unoccupied volume *inside* the bulb is 100-percent saturated air giving a small density difference between inside and outside air. The appropriate relationship is

$$m_{td} = m_{od} + (285 - m_{od}) \times 8 \times 10^{-6} \qquad (9)$$

where m_{td} is the true mass of distilled water, m_{od} is the mass obtained using (8), 285 cm^3 is the bottle volume, and 8×10^{-6} g/cm^3 is the density difference between inside saturated and outside (25-30‰ RH) air.

The appropriate amount of standard seawater was then added and the total mass of solution (weighed after mixing to ensure a uniform solution of known density [10]) was determined as for the distilled water. The salinity of the final solution was calculated after weighing from the relation

$$S = \frac{S_o}{1 + (m_{fd}/m_{ts})} \qquad (10)$$

where m_{fd}, m_{ts} are the true masses of distilled water and the final solution and S_o is the salinity of the standard seawater used ($S_{P79} = Cl_{P79} \times 1.806550 = 19.4360‰ \times 1.806550) = 35.00371‰$.

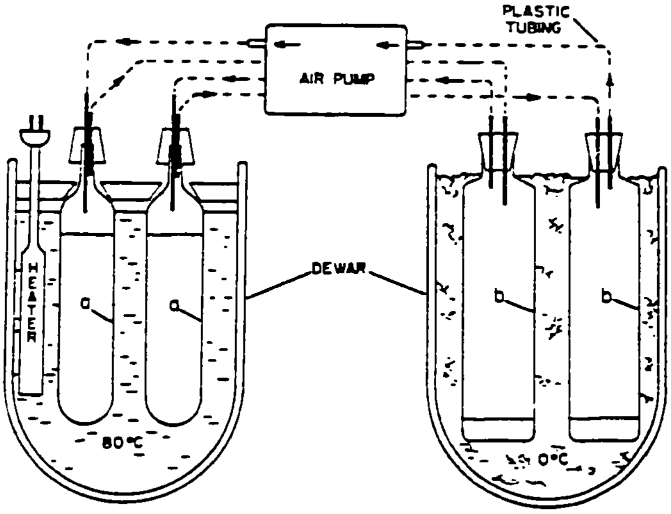


Fig. 5. The evaporation system for making >35‰ S solutions. The evaporating flasks (4a) are made from seawater ampoules, the condensers (also 4b) from 8-oz "packer" bottles. The aquarium pump is a vibrator type with no lubricated parts (Hush II modified for closed loop recirculation).

The purpose of this order of preparation was to ensure that no net evaporation occurred from the standard seawater as a result of handling before weighing. The slight evaporation of distilled water to saturate the airspace is accounted for by weighing after saturation and net evaporation from the salt water is prevented by its always being exposed to saturated air. Any water vapor carried out of the bottle with the air as the bottle is filled is allowed for in the weighing calculations.

The type 2 high salinity solutions (above 35‰) were prepared by dilution as necessary to an approximately known salinity from stock solutions made by evaporating standard seawater at elevated temperatures in a closed loop air recirculation system. Air circulation was provided by a small diaphragm type aquarium pump adapted to provide both air inlet and outlet connections (see Fig. 5). The air from the pump passed through eight bottles in series joined by plastic tubes and alternating between a hot (≈80°C) bath and a cold bath (crushed ice) before returning to the pump. The air inlet to each ampoule or bottle was jetted downward and a bit to one side to ensure good circulation against the evaporation or condensation surfaces. With this system a concentration increase to about 42‰ S could be achieved in several hours.[3]

A reasonably reliable estimate of the salinity of the concentrated stock solutions (say about ±1‰) could be made from the change of level of the water in the ampoule, and this was sufficient to allow us to make up >35‰ samples of full ampoule volume (≈285 ml^3) at a number of salinities between 35 and 42‰ S.

The samples described above were used to determine the salinity scale above 35‰ S as described later. They were

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[3] We first tried, without any real expectation of success, to obtain accurate ratios by weighing before and after the evaporation but this proved not to be feasible at the evaporation rates required to obtain the large number of samples we needed. Low pressure "forced" evaporation resulted in a tendency to "bumping" with splashing of the salt water which subsequently dried leaving salt in undesirable locations.

first run in the conductivity apparatus to obtain the conductance reading at the two temperatures being studied using as little water as possible. By making sure that the immediately preceding water run through the cell was within 1 or 2 ppt of the same salinity, the required sample volume could be kept below 100 ml.

These pre-read samples were then used to make up type 3 solutions ($<35‰$ S) by first precisely weighing the ampoule and its contents to obtain the mass M_1 of solution and then diluting the solution as previously described with distilled water to a salinity below 35‰, and a sample volume not less than 200-220 ml. The range of these diluted salinities was 28 to 35‰. The bottle and contents were again precisely weighed to obtain the new mass M_2 of solution and the dilution ratio M_1/M_2 was calculated.

The chief problem in carrying out the dilution experiments concerns prevention of evaporation from the solutions. Evaporation, say to saturate the air in the bottle, is not a problem with distilled water, provided the weighing is done after the evaporation has taken place and the appropriate allowance is made in the corrections for the difference in humidity between inside and outside. The salt water, on the other hand, changes concentration if any evaporation takes place and can easily increase salinity by 0.001‰S by evaporation into the remaining space in a dry container. Therefore, we adopted the practice of adding the distilled water first and weighing after the air was saturated. In the higher salinity ($>35‰$) measurements we also made a slight correction for the water carried out of the ampoule by air expansion when the driving pressure was released after the first measurement, but could ignore initial evaporation because all conductivity measurements came after.

The weighings described here were carried out on ampoules with a sealed cap on them to prevent evaporation between filling and weighing (they were done in lots of 12 bottles), during weighing, and in transfer to the room where the conductivity measurements were made. Therefore, a slight density correction was required for the small but consistent difference in temperature between filling and weighing. This correction was shown mathematically and experimentally to be to sufficient accuracy proportional to salinity and was taken care of in a final scaling of the data to make $S = 35‰$ correspond exactly to $R = 1$.

The balance used was a Mettler (type B5C1000) borrowed from the Metrology group of NRC. It has an extremely well-documented history and calibration corrections, being normally used in calibration of other balance weights. The ampoules were weighed resting on a light metal frame on the balance pan. They were filled via a fine Teflon tube using air pressure to drive the standard seawater directly from the original ampoule to the measuring one, or the distilled water from a 500-ml bottle. The lower salinity samples were prepared in lots of about 12 bottles spaced at appropriate intervals of salinity from 35‰ to 1 or 2‰, and were read sequentially so that consecutive samples would never be more than about 4‰ different. The sequence order was reversed each time to ensure that no systematic error due to constant salinity difference from preceding samples could occur.

MEASUREMENT PROCEDURE

The procedure in taking measurements is essentially the same as described by Dauphinee and Klein in an earlier paper [8]. The filled ampoule was first thoroughly mixed after replacing its sealing cap by a flat sheet of neoprene pressed against the end of the fill tube. The sheet (≈8-mm disk) was mounted in a blind hole in a rubber stopper and could be held in place with the index finger while imparting a rotary motion by wrist action. Prior to each use the stopper was flooded with a jet of distilled water to remove residual salt and blown dry with an air jet. After ensuring the neck was free of water the stopper was removed and replaced by a guide and seal assembly which allowed the fine Teflon inlet tube to the water flow system to pass through it to the bottom of the ampoule and formed an air seal to allow pressure buildup in the ampoule when pressed into a mating recess in the apparatus. The air pump was then turned on and a continuous flow of sample water was driven by air pressure through the Teflon feedline to a T connection where the flow was divided between the two cells. The flow was adjusted with a bypass valve to a 1/2 to 1 cm^3/s, a rate which allowed filling of the cells in 10-15 s but slow enough to allow a number of preliminary flushes (usually 5-7) and at least 4 readings on each cell (alternating between cells and with a flush every 2 readings) with a total flow of 150-200 ml. At frequent intervals the bath temperatures were measured. The circulating air was turned off, the ampoule removed, and the flow tube wiped clean to remove any traces of salt.

For salinity differences between consecutive samples of 4‰ or less the above procedure was repeated with the next sample. For greater differences a part bottle of synthetic seawater of about the same salinity was put through first as a precaution. After a temperature change an hour or two was allowed for bath control system stabilization before readings were taken. In every case one bath N (normal) was at 15°C and the other V (variable) was at some other temperature (−2, 0, 5, 10, 20, 25, 30, or 35°C). Consequently we obtained a 15°C reading for every reading at any other temperature, and the crucial $R_{t,15,0}$ versus S equation is based on 116 measured points (Table I) while the corresponding V bath readings are distributed over 8 different temperatures (Tables II-IX). This is an acceptable ratio since the constants of $f_2(R_t, t)$ (5), which express the result of a temperature deviation from 15°C are based on the whole $t \neq 15°\text{C}$ set.

Standardizations against standard water P79 were carried out in much the same way, except that the sealed ampoule was mixed by shaking (rotary motion for best stirring) before being opened at one end. The conductance cells were usually exchanged between the two baths, using a second ampoule if one was not sufficient, in order to check the ratio of the cell constants as discussed in Appendix-1) and [8].

SETTING UP THE SALINITY SCALE

The procedure in setting up the final salinity versus conductivity ratio scale based on seawater lot P_{79} consisted

TABLE I
THE MEASUREMENTS AT 15°C

	$R_{s,15,o}$	S_m	S_c	ΔS		$R_{s,15,o}$	S_m	S_c	ΔS
1	0.0380189	1.0354	1.0353	1	61	0.8808953	30.3833	30.3838	-5
2	0.0385086	1.0494	1.0493	1	62	0.8955899	30.9487	30.9482	5
3	0.0388800	1.0599	1.0599	0	63	0.8967724	30.9939	30.9937	2
4	0.0553164	1.5362	1.5362	0	64	0.8987789	31.0711	31.0708	3
5	0.0680156	1.9111	1.9111	0	65	0.8991950	31.0873	31.0869	4
6	0.0713993	2.0118	2.0119	-1	66	0.9162460	31.7439	31.7439	0
7	0.0883185	2.5209	2.5209	0	67	0.9210414	31.9290	31.9291	-1
8	0.1083350	3.1328	3.1328	0	68	0.9412842	32.7125	32.7124	1
9	0.1096210	3.1725	3.1724	1	69	0.9442486	32.8276	32.8273	3
10	0.1114450	3.2285	3.2287	-2	70	0.9462320	32.9044	32.9043	1
11	0.1364996	4.0087	4.0088	-1	71	0.9484356	32.9899	32.9898	1
12	0.1373610	4.0357	4.0359	-2	72	0.9487948	33.0037	33.0037	0
13	0.1735556	5.1846	5.1844	2	73	0.9498290	33.0435	33.0439	-4
14	0.2003220	6.0477	6.0476	1	74	0.9572872	33.3331	33.3336	-5
15	0.2017281	6.0940	6.0933	7	75	0.9693643	33.8045	33.8035	10
16	0.2285480	6.9692	6.9692	0	76	0.9758136	34.0546	34.0549	-3
17	0.2291836	6.9903	6.9901	2	77	0.9764668	34.0805	34.0803	2
18	0.2553445	7.8537	7.8540	-3	78	0.9853435	34.4275	34.4268	7
19	0.2589858	7.9747	7.9749	-2	79	0.9918971	34.6831	34.6829	2
20	0.3040306	9.4838	9.4838	0	80	0.9933003	34.7373	34.7378	-5
21	0.3186162	9.9773	9.9773	0	81	0.9995070	34.9813	34.9807	6
22	0.3192623	10.0001	9.9992	9	82	1.0029358	35.1148	35.1150	-2
23	0.3299615	10.3631	10.3627	4	83	1.0110922	35.4345	35.4348	-3
24	0.3477559	10.9697	10.9698	-1	84	1.0121222	35.4752	35.4752	0
25	0.3646323	11.5487	11.5486	1	85	1.0144113	35.5644	35.5650	-6
26	0.3811481	12.1176	12.1177	-1	86	1.0225050	35.8830	35.8829	1
27	0.3822646	12.1559	12.1563	-4	87	1.0241865	35.9486	35.9491	-5
28	0.4045831	12.9296	12.9297	-1	88	1.0251097	35.9858	35.9854	4
29	0.4355710	14.0108	14.0111	-3	89	1.0264604	36.0373	36.0385	-12
30	0.4420962	14.2399	14.2399	0	90	1.0311117	36.2220	36.2215	5
31	0.4771066	15.4740	15.4739	1	91	1.0319584	36.2549	36.2548	1
32	0.4866104	15.8101	15.8106	-5	92	1.0361935	36.4216	36.4217	-1
33	0.4878325	15.8538	15.8540	-2	93	1.0366625	36.4396	36.4401	-5
34	0.5311146	17.3973	17.3974	-1	94	1.0505861	36.9893	36.9894	-1
35	0.5475348	17.9869	17.9869	0	95	1.0592428	37.3312	37.3316	-4
36	0.5477041	17.9930	17.9930	0	96	1.0593876	37.3370	37.3373	-3
37	0.5754861	18.9945	18.9951	-6	97	1.0695130	37.7385	37.7382	3
38	0.6003925	19.8981	19.8987	-6	98	1.0729762	37.8753	37.8755	-2
39	0.6018951	19.9531	19.9533	-2	99	1.0748211	37.9485	37.9486	-1
40	0.6371108	21.2392	21.2392	0	100	1.0777718	38.0660	38.0657	3
41	0.6578729	22.0016	22.0015	1	101	1.0808476	38.1874	38.1877	-3
42	0.6643417	22.2394	22.2397	-3	102	1.0886694	38.4986	38.4985	1
43	0.6653720	22.2778	22.2777	1	103	1.0919088	38.6270	38.6273	-3
44	0.6835169	22.9480	22.9475	5	104	1.0995552	38.9312	38.9316	-4
45	0.6959100	23.4065	23.4064	1	105	1.1023667	39.0434	39.0436	-2
46	0.7104462	23.9462	23.9460	2	106	1.1072282	39.2372	39.2374	-2
47	0.7109785	23.9661	23.9658	3	107	1.1120131	39.4284	39.4283	1
48	0.7483693	25.3609	25.3609	0	108	1.1169082	39.6238	39.6237	1
49	0.7641955	25.9544	25.9544	0	109	1.1262677	39.9981	39.9978	3
50	0.7644542	25.9641	25.9641	0	110	1.1315109	40.2078	40.2077	1
51	0.7644606	25.9642	25.9643	-1	111	1.1571840	41.2382	41.2379	3
52	0.7725110	26.2671	26.2669	2	112	1.1623625	41.4455	41.4462	-7
53	0.7738373	26.3166	26.3168	-2	113	1.1656287	41.5785	41.5777	8
54	0.8167979	27.9397	27.9394	3	114	1.1692883	41.7250	41.7251	-1
55	0.8337167	28.5817	28.5819	-2	115	1.1718841	41.8297	41.8297	0
56	0.8435739	28.9573	28.9571	2	116	1.1787335	42.1063	42.1060	3
57	0.8441499	28.9792	28.9790	2					
58	0.8476656	29.1135	29.1131	4					
59	0.8489707	29.1630	29.1628	2					
60	0.8688527	29.9225	29.9224	1					

essentially of five parts:

1) The setting up of a salinity scale for $T = 15$°C and $S \leqslant 35$‰, based on the type 1 dilution samples,
2) the extension of the 15°C scale to higher salinities (up to 42‰) using the $<$35‰ scale already established and the dilution ratios obtained from the type 2 and type 3 samples (see (4)),
3) the use of the salinities computed from the 15°C scale and the measurements at 15°C along with the corresponding readings on the same samples at other temperatures to establish the scale over the whole t, R versus S plane (see (5)),
4) the derivation of constants for (1), the effect of temperature on the conductivity of standard seawater, using the data obtained in the cell standardizations carried out for the other measurements,
5) a mathematical analysis of the whole set of data to determine the form of equations which would give the most satisfactory and convenient fit.

Table I gives the results of all our measurements in the 1–42‰ range at 15°C. The first two columns are our measured conductivity ratio ($R_{s,15,o}$) and the corresponding weight determined salinity both based on P$_{79}$ but corrected to 35‰ (correction factor $C_{35,t,o}/C_{P79,t,o}$ = 0.9999054

TABLE II
THE MEASUREMENTS AT −2°C

	$R_{s,-2,o}$	ΔS_m	ΔS_c	ΔS
1	0.0372242	0.0228	0.0246	-18
2	0.0666786	0.0398	0.0410	-12
3	0.1349875	0.0745	0.0752	-7
4	0.2517345	0.1199	0.1196	2
5	0.3779667	0.1484	0.1476	8
6	0.4821931	0.1566	0.1555	11
7	0.5962733	0.1497	0.1486	11
8	0.6923535	0.1317	0.1305	12
9	0.7614789	0.1117	0.1107	10
10	0.8414327	0.0816	0.0808	8
11	0.8844520	0.0623	0.0617	6
12	0.8940929	0.0576	0.0572	4
13	0.9191935	0.0453	0.0448	5
14	0.9434155	0.0323	0.0321	2
15	0.9525967	0.0275	0.0272	3
16	0.9793380	0.0125	0.0122	3
17	1.0112520	−0.0062	−0.0068	6
18	1.0367580	−0.0222	−0.0227	5
19	1.0760309	−0.0479	−0.0487	8
20	1.1284167	−0.0860	−0.0859	-1

TABLE III
THE MEASUREMENTS AT 0°C

	$R_{s,0,o}$	ΔS_m	ΔS_c	ΔS
1	0.1711839	0.0760	0.0767	-7
2	0.2263350	0.0936	0.0941	-5
3	0.3152395	0.1145	0.1151	-6
4	0.3610786	0.1221	0.1226	-5
5	0.4009335	0.1268	0.1272	-4
6	0.5439276	0.1297	0.1299	-2
7	0.6804781	0.1124	0.1126	-2
8	0.7857326	0.0862	0.0865	-3
9	0.8476300	0.0656	0.0661	-5
10	0.8662802	0.0588	0.0592	-4
11	0.8867685	0.0512	0.0512	0
12	0.9189819	0.0375	0.0379	-4
13	0.9455637	0.0259	0.0262	-3
14	0.9790982	0.0097	0.0104	-7
15	0.9792666	0.0095	0.0103	-8
16	0.9995058	0.0003	0.0003	0
17	1.0122984	−0.0069	−0.0063	-6
18	1.0268252	−0.0143	−0.0139	-4
19	1.0512851	−0.0276	−0.0271	-5
20	1.1009717	−0.0564	−0.0558	-6
21	1.1595029	−0.0933	−0.0924	-9

TABLE IV
THE MEASUREMENTS AT 5°C

	$R_{s,5,o}$	ΔS_m	ΔS_c	ΔS
1	0.0380891	0.0121	0.0128	-7
2	0.0391182	0.0123	0.0131	-8
3	0.1086019	0.0314	0.0319	-5
4	0.3020382	0.0673	0.0678	-5
5	0.4856127	0.0787	0.0792	-5
6	0.5289279	0.0783	0.0787	-4
7	0.6351387	0.0722	0.0726	-4
8	0.7468039	0.0586	0.0587	-1
9	0.8325846	0.0430	0.0430	0
10	0.8857150	0.0313	0.0311	2
11	0.9156264	0.0240	0.0237	3
12	0.9406767	0.0169	0.0171	-2
13	0.9408406	0.0173	0.0170	3
14	0.9579341	0.0123	0.0123	0
15	0.9762772	0.0074	0.0071	3
16	0.9884537	0.0037	0.0035	2
17	1.0253006	−0.0071	−0.0079	8
18	1.0783994	−0.0249	−0.0256	7
19	1.1178976	−0.0395	−0.0398	3
20	1.1670766	−0.0584	−0.0587	3

TABLE V
THE MEASUREMENTS AT 10°C

	$R_{s,10,o}$	ΔS_m	ΔS_c	ΔS
1	0.0355729	0.0052	0.0055	-3
2	0.0356155	0.0052	0.0055	-3
3	0.0710674	0.0099	0.0101	-2
4	0.1359465	0.0173	0.0176	-3
5	0.2043420	0.0241	0.0241	0
6	0.2581446	0.0280	0.0282	-2
7	0.3302475	0.0322	0.0324	-2
8	0.3801670	0.0338	0.0344	-6
9	0.4199591	0.0350	0.0354	-4
10	0.4393567	0.0354	0.0357	-3
11	0.4726899	0.0358	0.0361	-3
12	0.4903705	0.0354	0.0361	-7
13	0.5072620	0.0357	0.0361	-4
14	0.5464458	0.0354	0.0357	-3
15	0.6009643	0.0338	0.0344	-6
16	0.6298045	0.0331	0.0333	-2
17	0.6466406	0.0325	0.0326	-1
18	0.6555805	0.0315	0.0322	-7
19	0.6828256	0.0307	0.0308	-1
20	0.7102036	0.0287	0.0292	-5
21	0.7622578	0.0248	0.0256	-8
22	0.8162468	0.0209	0.0211	-2
23	0.8439562	0.0180	0.0185	-5
24	0.8730245	0.0157	0.0156	1
25	0.8812539	0.0146	0.0147	-1
26	0.8878111	0.0142	0.0140	2
27	0.8950070	0.0135	0.0132	3
28	0.8985567	0.0128	0.0128	0
29	0.9202600	0.0103	0.0103	0
30	0.9369250	0.0082	0.0083	-1
31	0.9474174	0.0055	0.0070	-15
32	0.9509089	0.0059	0.0065	-6
33	0.9516330	0.0061	0.0064	-3
34	0.9598492	0.0055	0.0054	1
35	0.9733760	0.0040	0.0036	4
36	1.0029482	−0.0005	−0.0004	-1
37	1.0596048	−0.0085	−0.0087	2
38	1.1076301	−0.0161	−0.0164	3
39	1.1725624	−0.0274	−0.0278	4

for all t). The third column gives the salinity calculated from an equation of the form

$$S = \begin{cases} f_1(R) = \sum_{n=0}^{5} a_n R^{n/2}, \quad \text{where } R = R_{s,15,o}, \\ a_0 + a_1 R^{1/2} + a_2 R + a_3 R^{3/2} + a_4 R^2 + a_5 R^{5/2} \end{cases} \tag{4a}$$

which has been fitted to the measured points by the method of least squares with the condition $R_{35,15} = 1$. The values $a_0 - a_5$ are given in Table X. The final column gives the differences between measured and calculated values of $S \times 10^4$.

The precision with which this equation fits the data ($\sigma = 3.6 \times 10^{-4}$‰) is sufficient justification for its use. It has no real theoretical base although there is some for a series in $S^{1/2}$ (which incidentally does not work as well). It is however also a very fine verification of the reproducibility and precision of our equipment, substantially better than we had expected at the beginning of the tests. We were in fact led to this form of equation from the normal power series because the low scatter of the data allowed us to see the effects of the different terms of even a 9th degree polynomial, also fitted by least squares. Fig. 6 shows the improvement in fit at 15°C that is obtained by the 5th degree equation in $R^{1/2}$ over 5th, 7th, and 9th degree equations in R.

Tables II to IX give the data for the other temperatures in a different format. The measured value Δs_m is now the

TABLE VI
THE MEASUREMENTS AT 20°C

	$R_{s,20,o}$	ΔS_m	ΔS_c	ΔS
1	0.0393337	−0.0047	−0.0051	4
2	0.1146701	−0.0128	−0.0130	2
3	0.2031816	−0.0202	−0.0204	2
4	0.3310028	−0.0272	−0.0276	4
5	0.4437373	−0.0301	−0.0305	4
6	0.5565445	−0.0297	−0.0302	5
7	0.6660889	−0.0264	−0.0270	6
8	0.7381194	−0.0227	−0.0233	6
9	0.7743830	−0.0205	−0.0210	5
10	0.8493609	−0.0149	−0.0153	4
11	0.8673368	−0.0133	−0.0137	4
12	0.8684103	−0.0129	−0.0137	8
13	0.8994687	−0.0105	−0.0108	3
14	0.9499681	−0.0054	−0.0056	2
15	0.9537812	−0.0050	−0.0052	2
16	0.9758900	−0.0029	−0.0028	-1
17	0.9867580	−0.0008	−0.0016	8
18	0.9933131	−0.0005	−0.0008	3
19	1.0310410	0.0028	0.0038	-10
20	1.0365605	0.0041	0.0045	−4
21	1.0806109	0.0094	0.0102	−8
22	1.1020402	0.0130	0.0132	-2
23	1.1687296	0.0224	0.0230	−6

TABLE VII
THE MEASUREMENTS AT 25°C

	$R_{s,25,o}$	ΔS_m	ΔS_c	ΔS
1	0.0392046	−0.0092	−0.0095	3
2	0.1122255	−0.0241	−0.0237	−4
3	0.2029030	−0.0382	−0.0379	-3
4	0.3314644	−0.0511	−0.0514	3
5	0.4437030	−0.0564	−0.0567	3
6	0.5565120	−0.0557	−0.0562	5
7	0.6656897	−0.0497	−0.0502	5
8	0.7735360	−0.0386	−0.0392	6
9	0.7750986	−0.0392	−0.0390	-2
10	0.8439900	−0.0289	−0.0293	4
11	0.8484070	−0.0283	−0.0286	3
12	0.8598240	−0.0263	−0.0268	5
13	0.8728969	−0.0241	−0.0247	6
14	0.8992970	−0.0199	−0.0201	2
15	0.9487150	−0.0109	−0.0108	-1
16	0.9710076	−0.0058	−0.0062	4
17	0.9754233	−0.0050	−0.0053	3
18	0.9899844	−0.0021	−0.0022	1
19	0.9919451	−0.0019	−0.0018	-1
20	1.0143288	0.0032	0.0032	0
21	1.0240464	0.0056	0.0054	2
22	1.0588980	0.0136	0.0137	-1
23	1.0725497	0.0169	0.0170	-1
24	1.0913584	0.0219	0.0218	1
25	1.1613553	0.0404	0.0408	−4

TABLE VIII
THE MEASUREMENTS AT 30°C

	$R_{s,30,o}$	ΔS_m	ΔS_c	ΔS
1	0.0358114	−0.0126	−0.0123	-3
2	0.0450152	−0.0154	−0.0150	−4
3	0.0723317	−0.0237	−0.0227	-10
4	0.1094302	−0.0338	−0.0325	-13
5	0.2019918	−0.0542	−0.0530	-12
6	0.3213769	−0.0717	−0.0710	-7
7	0.4793751	−0.0804	−0.0802	-2
8	0.5499011	−0.0790	−0.0791	1
9	0.6597981	−0.0709	−0.0711	2
10	0.7659524	−0.0561	−0.0563	2
11	0.8452197	−0.0408	−0.0409	1
12	0.8704804	−0.0344	−0.0352	8
13	0.8975140	−0.0285	−0.0286	1
14	0.9491832	−0.0150	−0.0150	0
15	0.9565077	−0.0124	−0.0129	5
16	0.9696030	−0.0093	−0.0091	-2
17	0.9894669	−0.0027	−0.0032	5
18	1.0223295	0.0070	0.0070	0
19	1.0879379	0.0291	0,0293	-2
20	1.1303935	0.0447	0.0451	-4

TABLE IX
THE MEASUREMENTS AT 35°C

	$R_{s,35,o}$	ΔS_m	ΔS_c	ΔS
1	0.0895154	−0.0363	−0.0343	-20
2	0.2308384	−0.0752	−0.0729	-23
3	0.3505090	−0.0943	−0.0925	-18
4	0.4334384	−0.1005	−0.0993	-12
5	0.5781841	−0.0977	−0.0973	−4
6	0.7126176	−0.0807	−0.0809	2
7	0.7660684	−0.0703	−0.0705	2
8	0.8478103	−0.0503	−0.0505	2
9	0.8478103	−0.0503	−0.0505	2
10	0.8819506	−0.0405	−0.0406	1
11	0.9270002	−0.0260	−0.0263	3
12	0.9576906	−0.0156	−0.0157	1
13	0.9622412	−0.0139	−0.0141	2
14	0.9746863	−0.0094	−0.0096	2
15	0.9994236	−0.0002	−0.0002	0
16	1.0000827	0.0003	0.0000	3
17	1.0001030	0.0003	0.0000	3
18	1.0316333	0.0128	0.0126	2
19	1.0688068	0.0280	0.0283	-3
20	1.1108278	0.0473	0.0472	1
21	1.1767680	0.0792	0.0794	-2

TABLE X
THE CONSTANTS FOR FUNCTIONS $f_1(R)$, $f_2(R)$, AND r_t

a_o = .00918	b_o = −.00018	c_o = .676615
a_1 = −.17694	b_1 = +.00079	$c_1 = 2.00568 \times 10^{-2}$
a_2 = 25.39560	b_2 = −.02838	$c_2 = 1.10295 \times 10^{-4}$
a_3 = 14.09878	b_3 = −.00197	$c_3 = -.68977 \times 10^{-6}$
a_4 = −7.03838	b_4 = +.03570	$c_4 = +.088 \times 10^{-8}$
a_5 = 2.71176	b_5 = −.00596	k = .016128
Σa_n = 35	Σb_n = 0	

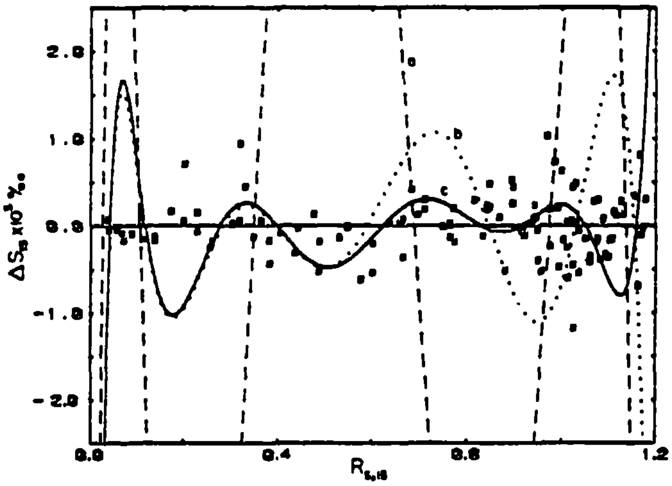

Fig. 6. Differences ΔS_{15} at 15°C between salinities given by the 5th degree equation in $R_{15}^{1/2}$ and the measured (by weighing) values, and also values calculated from (a) 5th, (b) 7th, and (c) 9th degree equations fitted by least squares.

difference between the weight determined salinity and the salinity calculated by substituting the "known" $R_{s,t}$ instead of $R_{s,15}$ in (7). The calculated value ΔS_c is the corresponding difference given by the correction function $f_2(R_{s,t,o},t)$ =

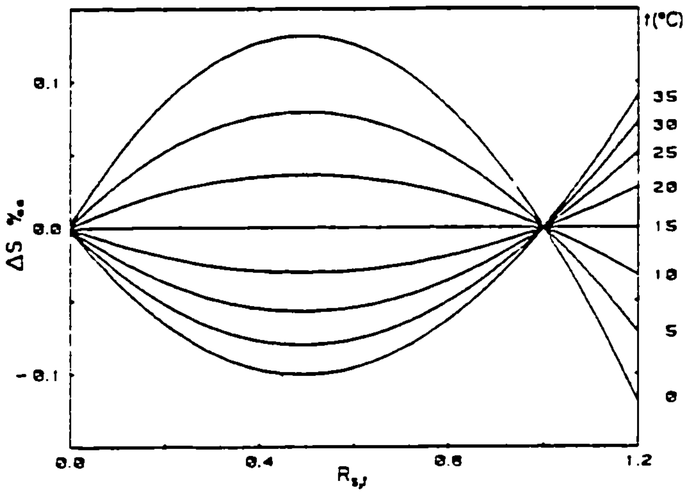

Fig. 7. The magnitude of the correction term

$$\Delta S = f_2(R_{s,t,o},t) = \frac{\Delta t}{1 + k\Delta t} \sum_{n=0}^{5} R_{s,t,o}{}^{n/2}$$

at the various temperatures as a function of $R_{s,t,o}$.

$-\Delta S_c$ which has been derived and fitted by least squares to correct for the error created by that substitution. It will be noted that f_2 expresses the correction for substitution of $R_{s,t,o}$ in units of ΔS rather than the previously used technique of correcting $R_{s,t,o}$ to $R_{s,15,o}$ before calculating S. It turns out that the correction is separable into the product of a simple expression in $\Delta t = (t - 15°\mathrm{C})$ and a function in $R_{s,t,o}$ having the same form as f_1. Therefore, the new S equation is

$$S = \begin{cases} \displaystyle\sum_{n=0}^{5} a_n R^{n/2} + \frac{\Delta t}{1 + k\Delta t} b_n R^{n/2}, \quad \text{where } R = R_{s,t,o} \\ \displaystyle\sum_{n=0}^{5} \left(a_n + \frac{\Delta t}{1 + k\Delta t} b_n \right) R^{n/2}. \end{cases} \tag{5a}$$

The complete set of constants is listed in Table X.

The magnitude of the correction term (ΔS_c) at the various temperatures and salinities is illustrated in Fig. 7. The differences between measured and calculated values at 15°C are shown in Fig. 6 and the differences at other temperatures in Fig. 8(a)-(h). The "best fit" constants (by least squares) determined from only the data at that temperature are quite different from the corresponding constants ($a_n + f(t)b_n$) of the general equation at the same temperature. This results from the fact that in a series of this type the constants are very sensitive to small changes of the values being fitted because of the great overlap of the range of effectiveness of adjacent terms. A substantial difference in one constant can be compensated quite accurately by changes in the constants further up in the series. However, the "best fit" constants are a significant improvement only at extremes of both temperature and salinity simultaneously.

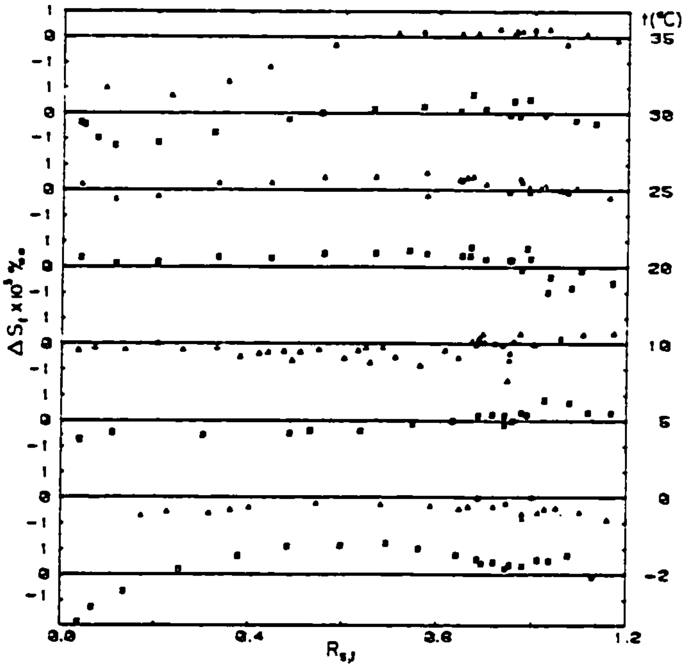

Fig. 8. Differences between measured and calculated salinities (using (8)) at −2, 0, 5, 10, 20, 25, 30, and 35°C.

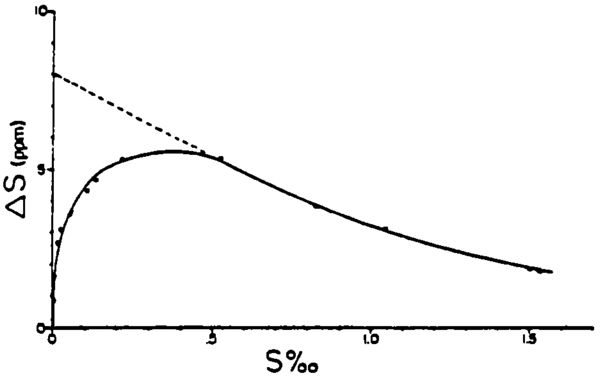

Fig. 9. The behavior of the $R_{s,15}$ versus S relationship at very low salinities. $\Delta S = S_c - S_m$ where S_c is based on the Brown-Allentoft low salinity equation.

MEASUREMENTS AT VERY LOW SALINITIES

The primary aim of this project has been to supply data for a practical salinity scale based on ocean water. For this the 1-42‰ range of the main measurements is more than sufficient and waters with salinities in the lower end, except possibly in the Arctic regions, will tend to have ionic distribution characteristic of some particular drainage system, not seawater. However, it was obvious that our data was not extrapolating naturally to $R_{s,15} = o$ at $S = o$ and a few measurements were undertaken at very low salinities and 15°C to study the shape of the curve as S approached 0. The two definitive runs are plotted in Fig. 9. Earlier preliminary measurements show a random scatter of ±1 ppm from this curve.

Fig. 9 shows the differences ΔS between salinities S_c calculated using Brown and Allentoft's [7] low salinity equation and the actual weight determined salinities S_m

plotted on a greatly expanded S scale. A double dilution process was used to obtain better low salinity resolution. It will be seen that the curve, which on the basis of the $S > 1‰$ data is extrapolating to +8 to 9 ppm S (see a_o Table X) at $R_{s,15} = o$, in fact turns down at lower salinities and extrapolates to $S \approx o$ at $R_{s,15} \approx o$ as one would expect for pure water. Our lowest reading at $S \approx 2$ ppm corresponds to a cell impedance of 2.5 MΩ and a water conductivity of 4×10^{-6} $(\Omega\ \text{cm})^{-1}$, only 4 to 5 times that of our air equilibrated distilled water.

A plot of all of the Brown and Allentoft data at low salinities (<4‰) by individual runs indicates that each run followed a similar curve but without getting to low enough salinities to show the downturn and with the individual runs displaced from one another, probably as a result of different origins of the samples, with a spread of about 6 ppm. The average is about 2-3 ppm lower than ours.

Our own 15°C equation can be extended to fit all of our data over the full $0 < S < 42‰$ range with no increase of σ by replacing a_o with the function

$$a_o \frac{(r + r^2)}{1 + (r + r^2)}, \qquad \text{where } r = R_{s,15,o}/0.0032.$$

We are continuing the investigation at very low salinities, particularly to study the effect of CO_2 content and temperature. The results will be reported later.

TABLE XI
THE MEASUREMENTS OF r_t

	t(°C)	$W_{35,t}$	r_t	Δr_t	ΔS_r
1	-2.0	0.636950	0.636948	2	1
2	-2.0	0.636954	0.636948	6	4
3	-2.0	0.636946	0.636948	-2	-1
4	0.0	0.676612	0.676615	-3	-2
5	0.0	0.676611	0.676615	-4	-2
6	0.0	0.676620	0.676615	5	3
7	0.0	0.676604	0.676615	-11	-7
8	5.0	0.779571	0.779571	0	0
9	5.0	0.779572	0.779571	1	1
10	5.0	0.779580	0.779571	9	5
11	5.0	0.779577	0.779571	6	3
12	10.0	0.887536	0.887532	4	2
13	10.0	0.887529	0.887532	-3	-1
14	10.0	0.887531	0.887532	-1	-0
15	10.0	0.887535	0.887532	3	1
16	10.0	0.887537	0.887532	5	2
17	20.0	1.116501	1.116492	9	3
18	20.0	1.116488	1.116492	-4	-1
19	20.0	1.116498	1.116492	6	2
20	25.0	1.236518	1.236536	-18	-6
21	25.0	1.236533	1.236536	-3	-1
22	25.0	1.236569	1.236536	33	11
23	25.0	1.236570	1.236536	34	11
24	25.0	1.236525	1.236536	-11	-4
25	25.0	1.236538	1.236536	2	1
26	25.0	1.236535	1.236536	-1	-0
27	30.0	1.359665	1.359674	-9	-3
28	30.0	1.359667	1.359674	-7	-2
29	30.0	1.359652	1.359674	-22	-6
30	35.0	1.485462	1.485461	1	0
31	35.0	1.485449	1.485461	-12	-3
32	35.0	1.485482	1.485461	21	6
33	35.0	1.485468	1.485461	7	2
34	35.0	1.485454	1.485461	-7	-2

THE DETERMINATION OF r_t

Conductivity cell standardizations were normally carried out against two bottles of standard seawater P79, the cells being exchanged between the two baths after the first bottle. This gave us a measurement of the cell constant for each cell at both temperatures and allowed us to calculate the ratio of the two cell constants (Appendix-1),(A2)) thus giving a check that no significant changes had occurred in one cell. With a knowledge of the cell ratio and correction for linear expansion of the Pyrex of the cells we could then determine the ratio of the conductivities of any sample of seawater at two precisely known temperatures, one always very close to 15°C.

The predetermined cell ratio and simultaneous readings on the two cells were always used, rather than consecutive readings of the same cell in the two baths, because a second sample of seawater and a significant time delay were required for an exchange reading, and variability of samples would cause increased scatter of the measurements. Reproducibility of the ratio of cell constants over short periods is of the order of a few parts per million.

From the data determined as above a set of 34 values of $W_{35,t} = R_{35,t}/R_{35,15}$ were obtained for the various standard temperatures used. (−2, 0, 5, 10, 20, 25, 30, and 35°C). These are listed in Table XI along with the values r_t given by a 4th degree equation in t, i.e.,

$$r_t = \sum_{n=0}^{4} c_n t^n \tag{1a}$$

which was fitted to the measured data by the method of least squares, with the condition that $r_{15} = 1$. The constants c_n are given in Table X. Our previous work on the effect of temperature on the conductivity of various seawaters [8] has shown that a 3rd degree equation is not sufficient and a 5th degree term is unnecessary. The final column of the table shows the difference between measured and calculated values expressed as an equivalent salinity error $\Delta s_r (\times 10^4)$. The standard deviation of the fit is $\sigma(r_t) = 1.2 \times 10^{-5}$: $\sigma(\Delta S) = 4.4 \times 10^{-4}‰$.

The values given by (1a) are in good, but not spectacular, agreement with our previous measurements on lot P69 standard seawater. The differences are of the order of 1.5-2.0 ppm S at 0 and 35°C, within the quoted accuracy (1.5-2 ppm S) of the earlier measurements alone. We believe the present measurements to within ±1 ppm S at the extremes and better than that at intermediate temperatures. Independent confirmation of this has been given by the most recent work of Bradshaw and Schleicher [4] (this issue) who have carried out a new careful determination of the variation of W_t with temperature at a number of salinities, including 35‰ exactly.

Their data for 35‰ lies between our two sets. A comparison of our present results with theirs is given in their paper (Fig. 4). A comparison with Brown and Allentoft and Reeburgh is given in their Fig. 5.

CONCLUSION

The constants given in Table X give all of the data required for the use of either $R_{s,t,o}$ or $W_{s,t,o}$ to calculate salinity anywhere over the S, t plane at normal pressures within the range $-2 < t < 35°$C and $1‰ < S < 42‰$, and using (5a). In the range covered by "real-life" ocean waters agreement between experiment and the equation has been spectacularly good, considering that the method of introducing temperature into the equation allows no latitude whatsoever for adjustments to improve the fit at a particular temperature. In effect, all the $T \neq 15°$C data has been treated as a single set and the excellent fit achieved in this way gives very great confidence that no part of the t, S plane has major errors in it. In addition there is independent confirmation by other workers [3], [4], [7] for all data for $S > 4‰$.

The work reported here has been used along with that of other laboratories in the development of the new Practical Salinity Scale 1978 [11], [12]. The constants given here give the best representation of our data *alone* and are not recommended for use by oceanographers in their normal work. The constants prescribed for the official scale [11] give results negligibly different from ours, and for the sake of consistency should always be used in reporting oceanographic data.

APPENDIX

Some additional technical considerations include the following.

1) A change of 1 ppm/°C in the apparent ratio of cell constants of two of the cells (with temperature but not with salinity) was traced to improper annealing of the cells. These were new cells made locally to replace the original pair, one of which had been broken. Annealed replacements made by Glass Craft, Toronto, gave no measurable dependence on either T or S. The expansion coefficient of Pyrex is well documented, the total correction for expansion for a cell (from its 15°C value) never exceeding 3 ppm S. Our procedure for determining the ratio between the cells is independent of expansion coefficient unless the cells are different [8]. Readings are taken on both cells at both temperatures t_1 and t_2 and then the cells are exchanged between baths and readings taken again with water of nearly the same salinity. If k is the expansion coefficient, α is the cell ratio for identical S and t of cells a and b, and C_a and C_b are the uncorrected cell conductances, i.e.,

$$\alpha = \frac{(C_a)_{s,t,o}}{(C_b)_{s,t,o}}$$

and $C_{s,t,o}$ is the true conductivity of seawater at temperature t, then for the exchange described above

$$\frac{C_{s,t_1,o}}{C_{s,t_2,o}} = \frac{(1 - k\Delta t)(C_a)_{s,t_1,o}}{\alpha (C_b)_{s,t_2,o}} = \frac{(1 - k\Delta t)\alpha(C_b)_{s,t_1,o}}{(C_a)_{s,t_2,o}} \tag{A1}$$

$$\alpha^2 = \frac{(C_a)_{s,t_1,o}\ (C_a)_{s,t_2,o}}{(C_b)_{s,t_1,o}\ (C_b)_{s,t_2,o}}. \tag{A2}$$

The required stability of the bath temperatures need only last a few minutes and is easily achieved.

2) After balancing the differential amplifier network, using resistors to simulate the cell, differences of amplifier frequency response left a slight unbalance, equivalent to about 1 ppm S, when a simulation circuit generated a waveform equivalent to the waveform actually seen at the current electrodes. This was eliminated by adding a small capacitance at the output of A_2 (Fig. 4).

3) Test 2) above led to investigation of the effects of platinizing the electrodes, since the slope of the polarization curve should be considerably reduced. We found that a reduction of about 15 to 20 times could be consistently maintained for an indefinite period with the methods of cell cleaning we now use.

4) A frequency change from f to $f/2$ gave a change of about 8 ppm (0.3 ppm S) in the measured conductance at normal salinities. The change was approximately proportional to the conductance and therefore has no effect on our results.

5) Insulation resistance to the bath was measured with the heat exchanger end of the cell (where leakage does not matter) sealed off. Even after long term immersion in the bath and filled with seawater the insulation value exceeded 400-600 MΩ, representing an error not more than 0.15 ppm S at salinities far from $35‰$ only.

6) A failure of readings at 50 to 100 ppm S was traced to a switching spike, due to ringing on reversal at high cell impedances, which overdrove the output FET switches. Overdriving was eliminated by reducing the power supply to amplifier A_7 (Fig. 4) to limit the spike. We also slowed the reversal slightly, and shifted the ON period of S_3 and S_4 back in time with respect to the reversal to give the ring more time to decay. Once this was done readings could be taken to about 1.5 ppm S at 15°C.

7) The suppression network (including the amplifiers) has been shown by autocalibration and other checks to have excellent linearity. The output gain (to the DVM) can be trimmed to $<2/10^4$ but once trimmed is stable to $1/10^5$ indefinitely and with a numerical correction for this (X 0.99987) the overall system is better than $\pm 2/10^6$ of full scale (0.1 ppm S). The cell selector switch also has positions for zero conductance (open circuit) and a stable 250-Ω resistor to allow determination of the zero offset of the output circuit and a check for overall sensitivity of the system.

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Conductivity/Salinity/Temperature Relationship of Diluted and Concentrated Standard Seawater

ALAIN POISSON

Abstract—**The conductivity ratio of diluted and concentrated standard seawater has been measured very accurately in a salinity range from 0 to 42‰ and at temperature from −1 to 30°C. All the data have been fitted into polynomials which are compared with previous data. The specific conductance of seawater is deduced and a polynomial for the full range of salinity and temperature is proposed. Data presented in this paper have been used, with those of Dauphinee presented in this issue, to elaborate the new "Practical Salinity Scale 1978."**

INTRODUCTION

THIS WORK, PART OF which was performed for our Ph.D. dissertation has been used together with that of Dauphinee *et al.* [1] to establish a new definition of salinity and a new relationship between seawater conductivity, salinity, and temperature; both of them were proposed by the "Joint Panel on Oceanographic Tables and Standards" (JPOTS); these relationships are presented by Lewis [2] in this issue.

The aim of our dissertation was to study the influence of the variations in the ionic composition which exist to various degrees in the world ocean and in estuaries, on the seawater conductivity/salinity/temperature/density relationship.

These variations in composition are necessarily relative to a reference composition; consequently, our study was centered on a model including standard seawater as a principal component. A preliminary study of several batches of standard seawater [3] has shown that, even for standard seawater, the conductivity/chlorinity relationship is not single-valued considering the accuracy of present measurements. This led us to propose a method to standardize standard seawater [3] relative to a solution of potassium chloride and a convention which defined the 35‰ salinity of standard seawater by its electrical conductivity relatively to a KCl solution [4].

As our study concerned seawaters with 0 to 35‰ salinity, intermediate salinities were obtained by diluting the reference standard seawater defined above with distilled water; thus all the solutions had the same relative chemical composition. Conductivity/salinity/temperature relationships were measured for diluted seawater which is the main component of the model of natural seawater.

This work was extended later on to waters with a salinity higher than 35‰ and the procedure was improved. We present here all of our experimental data relating conductivity, salinity, and temperature, as well as the polynomials that were developed in our laboratory. The conductivity ratios were measured for seawaters with a salinity between 0 to 42‰ approximately, and for temperatures between −1°C and 30°C. These data are compared here with those published in the literature. They are compared with those of Dauphinee in the Perkin and Lewis paper on synthesis of all of the data [5].

APPARATUS AND METHOD

Preparation of Diluted and Concentrated Seawaters

All the diluted seawaters were obtained from standard seawater P75 and from double distilled water previously set in equilibrium with the air of the laboratory. The dilutions were carried out in special 500-cm^3 flasks. The flasks, together with the ampoules of standard seawater and

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The author is with Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, Tour 24, 4, Place Jussieu, 75230 Paris Cedex 05, France.

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the distilled water used are placed in the balance room at least 15 h before performing the dilutions, so that they should be in equilibrium with the air of the room whose temperature and humidity are maintained constant. The distilled water is first introduced into the flask which was then carefully stopped up and weighed on a Mettler B5 C 1000 balance. The walls of the flask are rinsed with this distilled water up to a few centimeters from the stopper in order to saturate rapidly the enclosed air. The appropriate quantity of standard seawater is then introduced rapidly into the flask, by means of a PVC tube. The flask is closed immediately, then weighed on the same balance. The salinity of diluted seawater is easily obtained from that of standard seawater by using the ratio of weights of standard seawater and of the solution, taking into account the quantity of evaporated water in the flask and the quantity of vapor water displaced when introducing standard seawater.

Concentrated seawaters were obtained by evaporating standard seawater up to a salinity of about 42‰, then diluting it according to the method described above. The apparatus used for concentration is shown schematically in Fig. 1. Throughout the evaporation, the seawater is only in contact with the volume of air enclosed in the system, which avoids supersaturation with CO_2, and consequently precipitation of calcium carbonate. The salinity of the most concentrated seawater was estimated by means of a laboratory salinometer. The "estimated salinities" (preceding paragraph) of the diluted seawaters made from it, calculated by the above-mentioned method, and their respective measured resistances where then fitted in a polynomial:

$$S = A_0 + A_1 R^{1/2} + A_2 R + A_3 R^{3/2} \tag{1}$$

The salinity values were then scaled to true salinity by making $S = 35‰$ correspond to the resistance of standard seawater, based on P75. This plot is then readjusted at 35‰.

Measurement of Conductivity Ratios

Those determinations were carried out by means of a Jones-type bridge which measures directly the resistance $R(\Omega)$ of the solution [6].

$$R(\Omega) = a/\chi \tag{2}$$

where χ is the specific conductance ($\Omega^{-1} \cdot \text{cm}^{-1}$), and "$a$" ($\text{cm}^{-1}$) the cell constant at the temperature of measurement. Thus if the resistances of standard seawater and of diluted (or concentrated) seawater are measured under the same conditions, the conductivity ratio is given by the inverse of the measured resistance ratio.

Seawaters are transferred directly from the dilution flask into the conductivity cell via a PVC tube, avoiding bubbling. This manipulation is performed in a humid enclosure so as to limit evaporation in the cell as much as possible while it is rinsed 4 or 5 times before being filled.

The conductivity of an aqueous solution varies by about 2 percent/°C; therefore, the bath temperature must be as homogeneous and stable as possible, for the whole range of interest. We have developed in our laboratory an apparatus, described in detail elsewhere [19], which makes it possible to maintain a temperature between −2 and 40°C to $\pm 0.4 \cdot 10^{-3}$ °C.

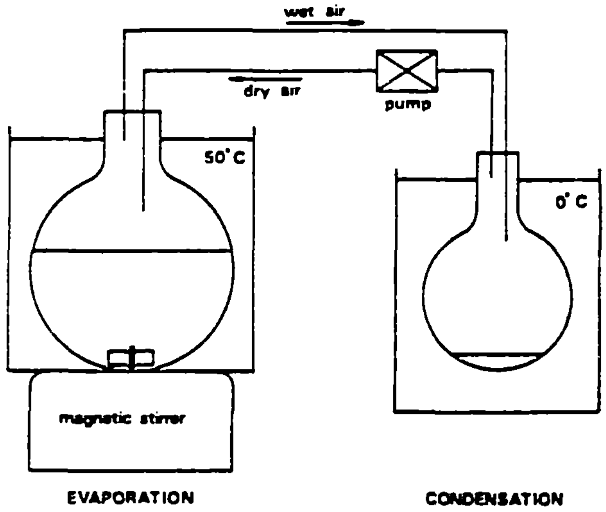

Fig. 1. Schematic diagram of apparatus used to concentrate standard seawater.

The Jones-type bridge and our procedure to measure the resistance of the solutions are described in the same UNESCO technical paper [19].

The resistances obtained are purely ohmic resistances with capacitance and self induction effects being eliminated by the well-known method of extrapolating to infinite frequency (ω) the straight line $R(\Omega)_{\text{measured}} = f(1/\omega)$.

TREATMENT OF RESULTS

Conductivity Ratios at 15°C

Poisson *et al.* [8] have shown that the electrical conductivity/chlorinity relationship of the different batches of standard seawater can vary slightly from one batch to another. This raises the problem of the choice of the salinity to be adopted for the standard seawater P75 used for the measurements presented in this paper. Since salinity is now determined from an electrical conductivity measurement, it is logical to try to find the relationship between these two parameters. But batch P75 is only standardized in chlorinity (Cl = 19.3740 ± 0.0003‰) by the standard seawater service. Therefore, we standardized it relatively to batches used in the intercomparison of different batches made previously [7]. Culkin (private communication) confirmed that its conductivity is just slightly above the average line $R_{15} = f(\text{Cl})$ where

$$R_t = (\chi_{\text{measured}}/\chi_{35‰}) \text{ at temperature } t \tag{3}$$

of the batches prepared at Wormley since 1974. Both the relationship of Cox *et al.* [8] ($S = 1.80655$ Cl) and that of Knudsen [9] ($S = 0.030 + 1.8050$ Cl) give a salinity of 35.0001‰ for a 19.3740‰ chlorinity. We have adopted

TABLE I

MEASURED DATA OF TEMPERATURE (°C). SALINITY ($^0/_{00}$). AND CONDUCTIVITY RATIO OF DIFFERENT SAMPLES INVESTIGATED

Temperature (°C)	Salinity ($^0/_{00}$)	Conductivity Ratio
30.0017	30.0478	0.873012
30.0017	25.0230	0.740915
30.0017	20.1911	0.610507
30.0017	14.9670	0.465019
30.0017	10.0215	0.322045
30.0017	6.1719	0.205843
30.0017	4.0684	0.139738
30.0017	30.0095	0.872024
30.0017	25.0074	0.740521
30.0017	19.9995	0.605248
30.0017	15.0141	0.466387
30.0017	9.9930	0.321209
30.0017	5.0260	0.170125
30.0017	34.9954	0.999876
30.0017	34.9849	0.999625
30.0017	37.4448	1.061587
30.0017	37.5256	1.063599
30.0017	39.0172	1.100815
30.0017	40.5543	1.138933
30.0017	41.0051	1.150048
24.9976	30.0202	0.872045
24.9976	24.9990	0.739864
24.9976	19.9902	0.604451
24.9976	14.9934	0.465126
24.9976	10.0465	0.322145
24.9976	5.9969	0.199964
24.9976	4.0410	0.138453
24.9976	29.9628	0.870587
24.9976	24.9772	0.739284
24.9976	19.9844	0.604258
24.9976	14.9842	0.464863
24.9976	10.0350	0.321843
24.9976	5.0759	0.171246
24.9984	41.5858	1.164815
24.9984	39.6100	1.115869
24.9984	38.4337	1.086534
24.9984	36.4373	1.036385
24.9984	34.9875	0.999682
20.0035	29.9938	0.871051
20.0035	24.8679	0.735824
20.0035	20.0005	0.603925
20.0035	15.0120	0.464928
20.0035	9.9426	0.318437
20.0035	6.0127	0.199874
20.0035	4.0634	0.138753
20.0035	30.0012	0.871256
20.0035	24.9075	0.736879
20.0035	20.0053	0.604123
20.0035	15.0048	0.464724
20.0035	9.9607	0.318929
20.0035	5.0602	0.170258
20.0021	41.4313	1.161483
20.0021	40.0680	1.127621
20.0021	38.6639	1.092554
20.0021	37.0106	1.050973
20.0021	34.9778	0.999435
15.0012	32.4731	0.935127
15.0012	29.9881	0.870591
15.0012	28.0543	0.819853
15.0012	25.0932	0.741224
15.0012	22.4491	0.670037
15.0012	20.3120	0.611742
15.0012	17.4156	0.531649
15.0012	14.8162	0.458511
15.0012	12.4784	0.391586
15.0012	9.9905	0.318987
15.0012	7.5308	0.245582
15.0012	6.0565	0.200581
15.0012	4.5068	0.152250
15.0012	32.2967	0.930563
15.0012	30.0339	0.871789
15.0012	27.9890	0.818125
15.0012	25.2659	0.745856
15.0012	22.4431	0.669874
15.0012	20.2692	0.610584
15.0012	17.5994	0.536771
15.0012	15.1242	0.467218
15.0012	12.3669	0.388364
15.0012	10.0021	0.319347
15.0012	7.5159	0.245126
15.0012	6.0375	0.199987
15.0012	4.3603	0.147642
15.0012	34.9884	0.999678
15.0012	34.9710	0.999258
15.0012	37.5027	1.063534
15.0012	38.9517	1.100069
15.0012	40.5259	1.139422
15.0012	41.7295	1.169348
15.0012	34.9942	0.999864
15.0012	34.9969	0.999925
15.0012	37.3845	1.060587
15.0012	38.9584	1.100185
15.0012	39.8064	1.121439
15.0012	41.0265	1.151893
9.9994	29.9844	0.870033
9.9994	25.0037	0.738059
9.9994	20.0230	0.602831
9.9994	15.0673	0.464577
9.9994	10.0138	0.318723
9.9994	5.0944	0.170074
9.9994	4.1130	0.139213
9.9994	30.0178	0.870909
9.9994	25.0006	0.737996
9.9994	20.0137	0.602577
9.9994	15.0762	0.464809
9.9994	9.9956	0.318181
9.9994	5.9490	0.196547
9.9994	4.0995	0.138805
10.0006	41.4145	1.162192
10.0006	40.1035	1.129397
10.0006	38.5247	1.089653
10.0006	36.4773	1.037740
10.0006	35.0089	1.000228
5.0019	30.0242	0.870578
5.0019	24.9280	0.735139
5.0019	22.5201	0.670066
5.0019	20.0431	0.602291
5.0019	17.3937	0.528774
5.0019	15.0916	0.464053
5.0019	12.1025	0.378521
5.0019	10.0373	0.318303
5.0019	5.9987	0.197184
5.0019	4.1290	0.139058
5.0019	30.0074	0.870125
5.0019	24.9541	0.735834
5.0019	22.5741	0.671528
5.0019	20.0358	0.602051
5.0019	17.4056	0.529126
5.0019	15.0998	0.464254
5.0019	10.0264	0.318003
5.0019	5.1327	0.170452
4.9987	40.7558	1.146415
4.9987	39.1240	1.105247
4.9987	37.2700	1.058142
4.9987	34.9938	0.999841
0.0027	30.2748	0.876584
0.0027	24.9904	0.735759
0.0027	19.8961	0.596834
0.0027	14.9730	0.459203
0.0027	10.0068	0.316054
0.0027	6.1337	0.200299
0.0027	4.1697	0.139515
0.0012	40.7391	1.146852
0.0012	39.1867	1.107453
0.0012	36.9453	1.050127
0.0012	34.9707	0.999241
−1.1047	30.0120	0.869544
−1.1047	24.9921	0.735548
−1.1047	20.0851	0.601747
−1.1047	14.9814	0.459095
−1.1047	10.0052	0.315716
−1.1047	6.0268	0.196808
−1.1047	4.2584	0.142138

the value 35.0000‰ as standard seawater salinity, the salinities of other seawaters being determined as discussed before. The maximum theoretical error in salinities due to errors in the weighings is always less than ±0.001‰S. The accuracy of the temperature measurement is ±0.001°C, but the precision of the measurement is 0.0002°C, and since conductivity ratios vary rather slowly with temperature, it is the precision which matters in our measurements.

Conductivity ratios of seawaters of salinity 4–42‰ were measured at temperatures ranging from −1°C to 30°C. The experimental data are listed in Table I.

The results obtained at 15°C have been used to calculate the polynomial coefficients of the relation

$$S = \sum_{n=1}^{8} A_n R_{15}{}^n \tag{4}$$

which has been normalized to give $S = 35.0000$‰ for $R_{15} = 1$. The coefficients are

$$\begin{aligned} A_1 &= 26.6963 & A_5 &= -168.1207 \\ A_2 &= 26.7686 & A_6 &= 130.8093 \\ A_3 &= -67.2337 & A_7 &= -56.3388 \\ A_4 &= 132.1490 & A_8 &= 10.2700 \end{aligned}$$

and the standard deviation is $\sigma = 4 \times 10^{-4}$‰.

A polynomial with only three coefficients was also developed, i.e.,

$$\begin{aligned} S = 35[&A_1(R_{15}{}^{5/2} - R_{15}) + A_2(R_{15}{}^2 - R_{15}) \\ &+ A_3(R_{15}{}^{3/2} - R_{15}) + R_{15}] \end{aligned} \tag{5}$$

where

$$\begin{aligned} A_1 &= 0.08887 \\ A_2 &= -0.2368 \\ A_3 &= 0.44499 \end{aligned}$$

and the standard deviation is $\sigma = 5 \times 10^{-4}$‰. We have chosen to develop these constrained polynomials giving $S = 0$ for $R_{15} = 0$ and $S = 35$ for $R_{15} = 1$ because the calculation of salinities from the weights of standard seawater and distilled water implies both constraints. In Table II we have compared salinities calculated with polynomial 5, to the mean salinities published by Brown and Allentoft [10], and to those calculated with the relations of Cox *et al.* [9].

$$\begin{aligned} S = &-0.08996 + 28.29720R_{15} + 12.80832R_{15}{}^2 \\ &- 10.67869R_{15}{}^3 + 5.98624R_{15}{}^4 - 1.32311R_{15}{}^5. \end{aligned} \tag{6}$$

We have also compared them to those calculated with the above polynomial 4 and those obtained with the Millero *et al.* [11] relationship

$$\begin{aligned} S = &27.25861R_{15} + 19.06186R_{15}{}^2 - 27.23835R_{15}{}^3 \\ &+ 27.09961R_{15}{}^4 - 14.19791R_{15}{}^5 + 3.01619R_{15}{}^6. \end{aligned} \tag{7}$$

The greatest differences are obtained with Cox salinities as expected. The latter measured the conductivity ratio and the chlorinity of numerous samples made by mixing samples from the all the world oceans and from different seas as well. The chlorinity measurements only took into account the halides brought by rivers, but not the nonhalide ions; therefore, the low salinities he calculated from chlorinity using the relationship $S = 1.80655$ Cl are lower than ours for a sample with the same conductivity. Brown [10] and Millero [11] obtained the whole range of salinities by diluting standard seawater with distilled water. It necessarily follows that our results are in better agreement with those of Brown and of Millero. We are in very good agreement with Brown and show slight deviations from Millero which are with a few exceptions within the combined experimental error of the two series of measurements. The differences arise from the fact that Millero measured conductivity ratios at 24°C and corrected them to 15°C by means of the relationship developed by Cox *et al.* [8]

$$\begin{aligned} R_{15} = R_t &+ 10^{-5}R_t(R_t - 1)(t - 15)[96.7 - 72.0R_t \\ &+ 37.3R_t{}^2 - (0.63 + 0.21R_t{}^2)(t - 15)] \end{aligned} \tag{8}$$

and that his measurement accuracy (standard deviation of the relationship 7 = 0.003‰) was less than ours (standard deviation of relationship 5 = 0.0005‰).

The influence of the form of the polynomials developed by the different authors is perceptible at very low and very high salinities. Polynomial 5—though containing the smallest number of constants—fits the Brown salinities best, even at extreme values. Brown average salinities used here were determined from salinities calculated with the different polynomials that he had established for each series of dilution; when a salinity range of the same series of dilutions was very wide, Brown developed two distinct polynomials, each of them only covering part of the studied salinities, in order to reduce the influence of the polynomial form on standard deviation. Consequently the difference between those average salinities and the salinities he measured is very small in the whole range of studied salinities.

For the remainder of this paper, we have used polynomial 5 to define the salinity obtained from R_{15} the conductivity ratio at 15°C.

Variation of the Conductivity Ratio with Temperature and Salinity

In routine measurements, seawater salinity is deduced from the conductivity ratio R_t measured either by means of a CTD probe at a temperature different from 15°C, or by means of a laboratory salinometer, many of which are not

TABLE II
SALINITY (‰) CALCULATED WITH POLYNOMIAL 5 AND DIFFERENCES (10^{-4} ‰) BETWEEN THIS SALINITY WITH SALINITY OF PREVIOUS WORKS OR WITH POLYNOMIAL 4

	$S_{\mathrm{pol.5}}$	$10^4 (S_{\mathrm{pol.5}} - S_{\mathrm{others}})$			
R_{15}	(‰)	Brown	Cox	Millero	$S_{\mathrm{pol.4}}$
0.00	0.0000	0	900*	0	0
0.05	1.3853	22	297*	−220	−88
0.10	2.8798	15	221	−120	−19
0.15	4.4359	0	262	−25	5
0.20	6.0377	−4	322	24	2
0.25	7.6768	−7	367	37	−5
0.30	9.3475	−2	386	26	−8
0.35	11.0461	3	380	7	−7
0.40	12.7699	5	354	−9	−3
0.45	14.5170	5	316	−16	1
0.50	16.2858	6	271	−13	3
0.55	18.0750	2	225	−4	2
0.60	19.8839	−7	182	11	0
0.65	21.7116	−6	144	26	−1
0.70	23.5576	12	113	38	−1
0.75	25.4214	6	87	43	0
0.80	27.3028	1	68	41	3
0.85	29.2015	−2	51	32	5
0.90	31.1174	1	36	20	5
0.95	33.0502	−2	19	8	3
1.00	35.0000	0	0	0	0
1.05	36.9667	2	−23	1	−1
1.10	38.9504	6	−49	13	3
1.15	40.9510	6	−76	35	5
1.20	42.9687*	13	−99*	61	−14

* Out of range.

thermostated at 15°C. In a first phase, we have developed a general relationship $S = f(R_t, t)$ including polynomial 5.

$$\begin{aligned} S = {} & 35[A_1(R_t^{5/2} - R_t) + A_2(R_t^2 - R_t) \\ & + A_3(R_t^{3/2} - R_t) + R_t] + R_t(R_t - 1)(t - 15) \\ & \cdot [B_0 + R_t^{1/2}(B_1 R_t + B_2 t) + tR_t^{1/2}(B_3 t + B_4 R_t^{1/2})] \end{aligned} \tag{9}$$

where A_1, A_2, and A_3 are the constants of polynomial 5, and the other constants are

$$B_0 = 3.57944 \times 10^{-2}$$

$$B_1 = -1.52869 \times 10^{-3}$$

$$B_2 = -1.43951 \times 10^{-3}$$

$$B_3 = 8.31376 \times 10^{-6}$$

$$b_4 = 7.25836 \times 10^{-4}.$$

The standard deviation is 1.0×10^{-3} ‰ between calculated values and measured values. This polynomial can be represented (Fig. 2) by a constraint surface bound in two regions:

- when $S = 0$, $R_t = 0$ whatever the temperature (AB on Fig. 2)
- when $S = 35$, $R_t = 1$ whatever the temperature (CD on Fig. 2).

This polynomial can be applied for $-1.1°\mathrm{C} < t < 30°\mathrm{C}$ and $0‰ < S < 41.5‰$.

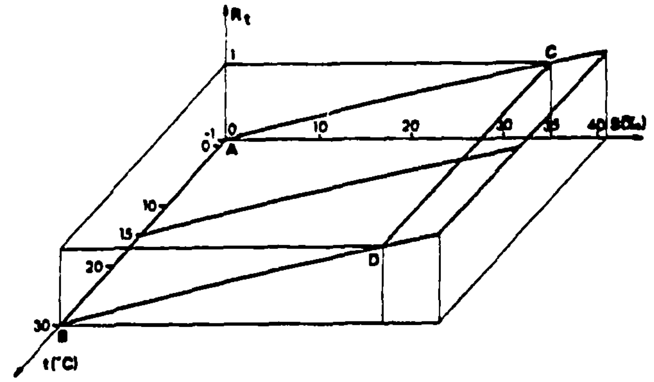

Fig. 2. Surface which represents the variation of salinity (S) versus conductivity ratio (R_t) of standard seawater solutions (polynomial 9).

The coefficients of the polynomials developed in this paper have been calculated by computing the minimum of the sum of deviation squares between values calculated from the polynomial and measured values. We have described this method in detail elsewhere [12]. To compare our conductivity ratios R_t with those existing in literature, we have calculated $\Delta_{15} = R_{15} - R_t$.

In order to reduce the influence of the form of the polynomial used to calculate Δ_{15}, we have calculated the coefficients of an inverse polynomial $R_t = f(S, t)$ using all the experimental data ($\sigma = 4 \times 10^{-5}$). R_{15} is calculated from this polynomial, and the differences $R_{15} - R_t$ are calculated for all the measured salinities and temperatures. Since the experimental error is very small compared to the

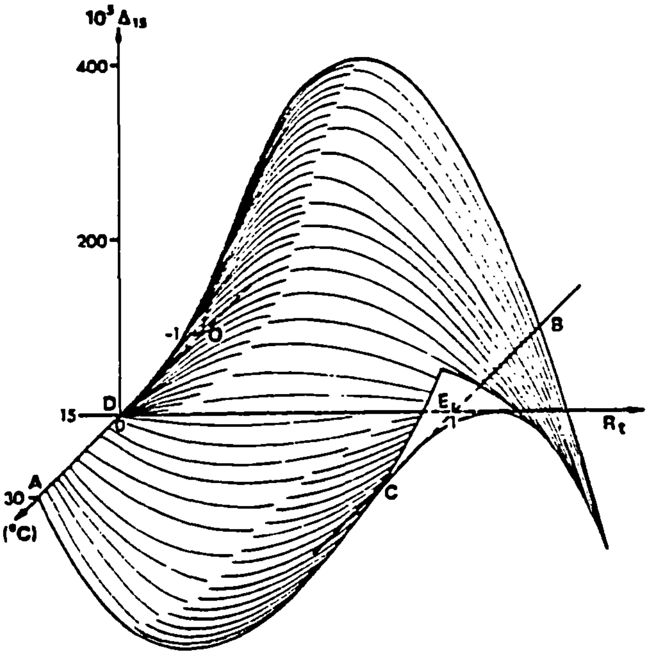

Fig. 3. Surface which represents the variation of $\Delta_{15} = R_{15} - R_t$ of standard seawater solutions (polynomial 10) versus temperature (t) and conductivity ratio (R_t).

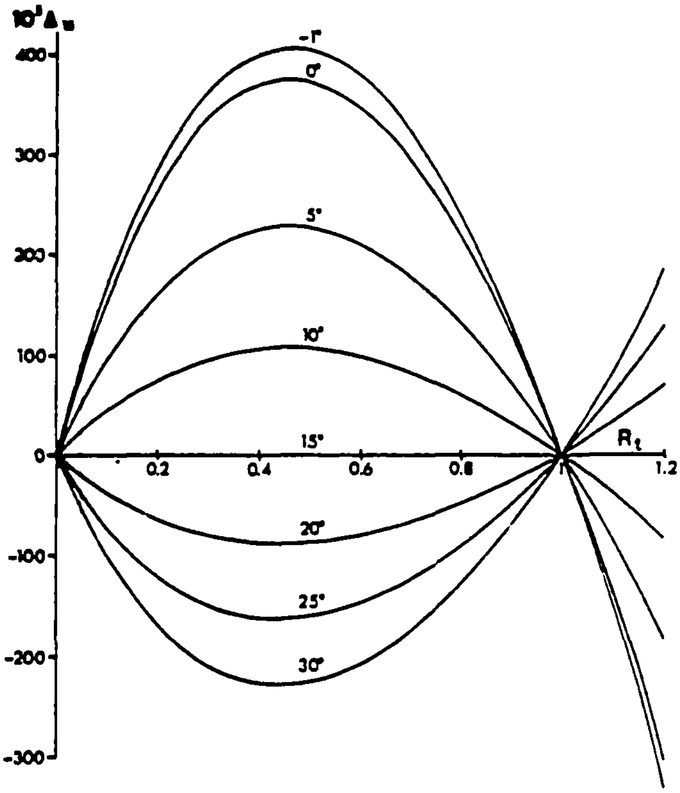

Fig. 4. Variation of Δ_{15} of standard seawater solutions (polynomial 10) versus conductivity ratio R_t at different temperatures.

value of the parameters used, we are perfectly justified in calculating for the mean surface $R_t = f(S, t)$ passing through experimental points; but the case is not the same for the differences $R_{15} - R_t$. As a matter of fact, near $R_t = 0$ and $R_t = 1$, the experimental error becomes greater compared to the differences $R_{15} - R_t$. Thus it is better to calculate these differences from a polynomial representing the surface $R_t = f(t, S)$ for a great number of points (all the temperatures and all the salinities of experimental points for instance) and to calculate the coefficients of a polynomial connecting $\Delta_{15} = R_{15} - R_t$ to R_t and to temperature. The surface representing this polynomial (Fig. 3) is bound in three regions:

- when $R_t = 0$, $\Delta_{15} = 0$ whatever the temperature. Therefore the surface passes through the segment OA of the temperature axis (Fig. 3)
- when $R_t = 1$, $\Delta_{15} = 0$ whatever the temperature; then the surface passes through BC
- when $T = 15$, $\Delta_{15} = 0$ whatever R_t; consequently, the surface must pass through DE. The polynomial representing this surface is of the form

$$10^5\Delta_{15} = R_t(R_t - 1)(t - 15)[120.0 - t(1.96 - 0.019t) - R_t(50.67 - 0.215\,t - 17.47\,R_t)] \quad (10)$$

and the standard deviation between measured values and calculated values is $\sigma = 0.3$.

The curves $\Delta_{15} = f(R_t)$ are represented for different temperatures on Fig. 4. To compare our results with those of Brown *et al.* [10] and those of Cox *et al.* [9] we have calculated the differences $\Delta = \Delta_{15}$ (Poisson) $- \Delta_{15}$ (other) at different temperatures. Cox proposed the polynomial

$$10^5\Delta_{15} = R_{15}(R_{15} - 1)(t - 15)[96.7 - 72.0\,R_{15} + 37.3\,R_{15}^2 - (0.63 + 0.21\,R_{15}^2)(t - 15)] \quad (11)$$

but Brown only presented his results under the form of a Table where Δ_{15} is given as a function of R_{15} at different temperatures. Thus we have fitted Brown's results for each temperature as a function of R_{15} (standard deviation between calculated values and measured values $\sigma = 0.5$); then we have calculated the differences $\Delta = \Delta_{15}$ (Poisson) $- \Delta_{15}$ (Brown) between 0 and 30°C. Though Cox polynomial was determined from experimental measurements carried out between 14 and 29°C, his polynomial was sometimes used in routine measurements at low temperatures. Thus we have also calculated the differences $\Delta = \Delta_{15}$ (Poisson) $- \Delta_{15}$ (Cox) between 0 and 30°C. These differences are presented on Fig. 5. Our results are in better agreement with Brown's results than with Cox's. This is due to the fact that Brown had prepared his samples by diluting seawater—previously concentrated by evaporation at a salinity of 50‰—with distilled water, whereas Cox had used samples coming from all the world oceans, low salinities being obtained by dilution with water from the Baltic. Of course in the temperature area that Cox did not study, i.e., on the extrapolation of his polynomial, this disagreement increases. The important deviations obtained for $R_t = 1.2$ are due to the fact that these values slightly exceed the salinity range studied. At low

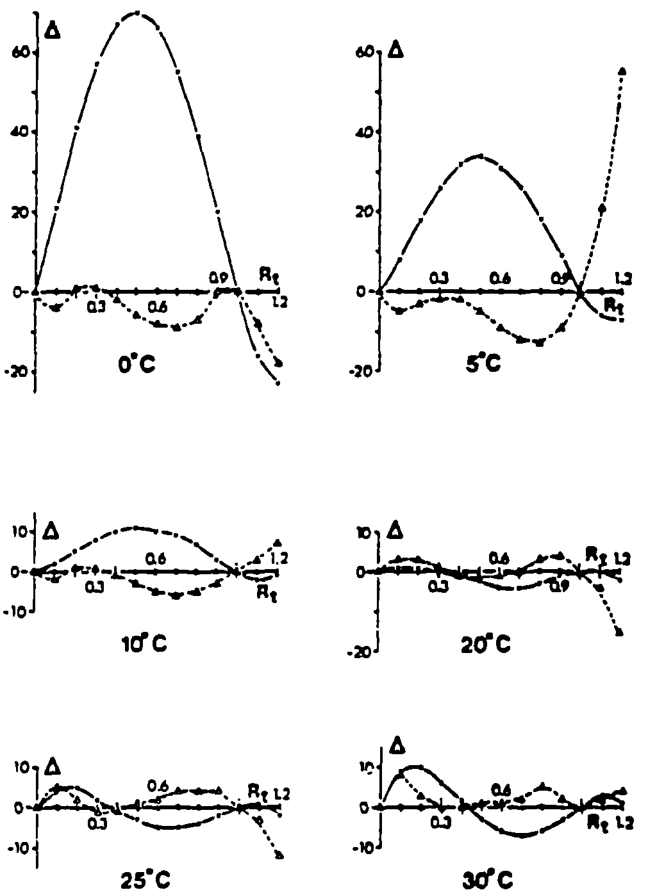

Fig. 5. Differences Δ(× 10^5) between Δ_{15} calculated with polynomial 10 and those determined by Cox *et al.* (1967) (·) or by Brown and Allentoft (1966) (▵) versus conductivity ratio at different temperatures.

temperatures the disagreement between Brown's results and ours is greater than experimental error.

Specific Conductance of Standard Seawater Solutions

Dauphinee and Klein [13] recently measured with very great accuracy the ratio of the conductivity of standard seawater of salinity 35‰ at t°C($\chi_{t,35}$) to that of the same seawater at 15°C($\chi_{15,35}$). They presented their results in the form of a fourth degree polynomial:

$$R_D = \frac{\chi_{t,35}}{\chi_{15,35}} = 0.6765836 + 2.005294 \times 10^{-2} t + 1.110990 \times 10^{-4} t^2 - 7.26684 \times 10^{-7} t^3 + 1.3587 \times 10^{-9} t^4. \tag{12}$$

At 25°C, this ratio is equal to

$$R_D = \frac{\chi_{25,35}}{\chi_{15,35}} = 1.236520. \tag{13}$$

Now standard seawater of batch P64 which has, at 25°C, a specific conductance based on standard KCl solutions of Jones [17] equal to 0.053084 $\Omega^{-1}\cdot\mathrm{cm}^{-1}$ [3]. For the same chlorinity this batch has a salinity deduced from conductivity smaller by 0.002‰ than the average for standard seawaters prepared since 1974 (Culkin private communication).

The variation of conductivity of standard seawater (35‰) is about $1.4 \times 10^{-6}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ for 0.001‰S [14], thus the specific conductance at 25°C of the water of batch P75 is 0.053087 $\Omega^{-1}\cdot\mathrm{cm}^{-1}$. The salinity of this batch P75 being exactly 35‰ the specific conductance at 25°C of standard seawater corrected to a salinity of 35‰ is thus equal to the above value. Hence, from 13

$$\chi_{15,35} = 0.042933\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$$

and from 12

$$\chi_{t,35} = 0.042933 R_D.$$

From experimental results listed in Table I and the value of $\chi_{t,35}$ mentioned above, we can easily obtain the specific conductance of diluted and evaporated seawater

$$\chi_{t,S} = R_t \chi_{t,35} = 0.042933 R_t R_D \tag{14}$$

for each temperature and experimental salinity.

The coefficients B_i of the polynomial

$$\chi_{t,S} = \frac{S}{35}(0.042933 R_D) + S(S-35)(B_0 + B_1 S^{1/2} + B_2 t + B_3 S + B_4 S^{1/2} t + B_5 t^2 + B_6 S^{3/2} + B_7 tS + B_8 t^2 S^{1/2}) \tag{15}$$

where R_D is polynomial 12 mentioned above have been calculated by the method of least squares:

$B_0 = -8.647 \times 10^{-6}$

$B_1 = 2.752 \times 10^{-6}$

$B_2 = -2.70 \times 10^{-7}$

$B_3 = -4.37 \times 10^{-7}$

$B_4 = 5.29 \times 10^{-8}$

$B_5 = -1.08 \times 10^{-9}$

$B_6 = 2.61 \times 10^{-8}$

$B_7 = -3.9 \times 10^{-9}$

$B_8 = 1.2 \times 10^{-10}$.

The absolute value of the mean standard deviation between the values calculated with this polynomial and the measured values is $3.10^{-6}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$.

It should be observed that the form of this polynomial permits us—if the conductivity of standard seawater at 15°C is measured with still greater accuracy in the future—to use the new value instead of 0.042933 $\Omega^{-1}\cdot\mathrm{cm}^{-1}$ which appears here. This polynomial can be represented with a surface passing through the temperature axis, since when $S = 0$, $\chi_{t,S}$ is the specific conductance of pure water which is about $1.10^{-6}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ at 25°C, and which accordingly can be put equal to zero in this calculation. The values given

TABLE III
SPECIFIC CONDUCTANCE ($\Omega^{-1}\cdot cm^{-1}$) OF STANDARD SEAWATER SOLUTIONS CALCULATED WITH POLYNOMIAL 15

Temperature	Salinity							
(°C)	5‰	10‰	15‰	20‰	25‰	30‰	35‰	40‰
0.0	0.004808	0.009171	0.013357	0.017421	0.021385	0.025257	0.029048	0.032775
2.5	0.005184	0.009884	0.014386	0.018753	0.023008	0.027163	0.031229	0.035222
5.0	0.005570	0.010616	0.015441	0.020118	0.024674	0.029120	0.033468	0.037734
7.5	0.005966	0.011365	0.016522	0.021517	0.026379	0.031123	0.035760	0.040306
10.0	0.006370	0.012131	0.017627	0.022947	0.028123	0.033171	0.038103	0.042935
12.5	0.006783	0.012912	0.018755	0.024406	0.029902	0.035261	0.040495	0.045619
15.0	0.007204	0.013709	0.019905	0.025894	0.031716	0.037391	0.042933	0.048355
17.5	0.007632	0.014521	0.021076	0.027408	0.033562	0.039559	0.045413	0.051138
20.0	0.008068	0.015346	0.022267	0.028948	0.035438	0.041762	0.047934	0.053968
22.5	0.008511	0.016185	0.023476	0.030511	0.037344	0.043999	0.050493	0.056840
25.0	0.008960	0.017035	0.024703	0.032097	0.039276	0.046267	0.053088	0.059751
27.5	0.009416	0.017898	0.025946	0.033703	0.041233	0.048564	0.055715	0.062700
30.0	0.009877	0.018771	0.027204	0.035330	0.043213	0.050888	0.058373	0.065683

TABLE IV
COMPARISON OF SPECIFIC CONDUCTANCE ($10^{-3}\ \Omega^{-1}\cdot cm^{-1}$) OF SEAWATER DETERMINED BY THOMAS ET AL. 1934 (TTU), OR REEBURGH, 1965 (R), AND THOSE CALCULATED WITH POLYNOMIAL 15 (P)

Cl	5.535‰		11.071‰		16.000‰			18.000‰			19.000‰			22.000‰		
S_K	10.021‰		20.013‰		28.910‰			32.520‰			34.325‰			39,740‰		
S_{Cox}	10.000‰		20.000‰		28.905‰			32.518‰			34.324‰			39.744‰		
	TTU	P	TTU	P	TTU	R	P	TTU	R	P	TTU	R	P	TTU	R	P
0°C	9.165	9.172	17.413	17.421	24.403	24.403	24.416	27.173	27.164	27.175	28.542	28.530	28.539	32.558	32.575	32.586
5°C	10.621	10.616	20.126	20.118	28.168	28.139	28.155	31.348	31.303	31.321	32.917	32.870	32.885	37.500	37.505	37.517
10°C	12.124	12.131	22.947	22.947	32.063		32.076	35.659		35.669	37.432		37.443	42.615		42.690
15°C	13.702	13.710	25.884	25.894	36.153	36.136	36.160	40.192	40.168	40.198	42.176	42.162	42.191	47.925	48.058	48.080
20°C	15.329	15.346	28.930	28.948	40.361		40.391	44.862		44.889	47.077		47.108	53.527		53.662
25°C	17.014	17.035	32.078	32.097	44.719	44.721	44.751	49.696	49.685	49.722	52.148	52.138	52.175	59.297	59.386	59.414
29°C		18.420		34.677		48.290	48.321		53.640	53.680		56.283	56.323		64.093	64.122

by this polynomial for various temperatures and salinities are listed in Table III.

We have compared our results with those of Thomas *et al.* [13] and those of Reeburgh [14]. One should note immediately that this comparison (Table IV) only has value for the order of magnitude of the different results. Thomas *et al.* have measured the conductivity of samples collected from the Indian and Pacific Oceans, the Mediterranean Sea, and the Gulf of Alaska at different depths, some diluted with distilled water.

Moreover they used the standards of Parker and Parker [16] whose values were slightly in error [17], and they measured the chlorinity of their solutions with respect to a solution of NaCl. Reeburgh measured the conductivity of samples of water from the Red Sea diluted with distilled water, but over a more restricted chlorinity range than that studied by Thomas *et al.* The Thomas *et al.* values of $\chi_{t,S}$ listed in Table IV were calculated using the interpolation relationships presented in their paper after transforming the present chlorinity into the equivalent of chlorine such as they measured it. Atomic weights of elements were redefined in 1940 and Reeburgh has shown that to obtain their equivalent of chlorine, we must multiply the present chlorinity by 1.00045. The Reeburgh values listed in Table IV are his interpolated values. Ours were calculated using polynomial 15 above, and $S = 1.80655$ Cl for the different chlorinities chosen for this comparison. We have also given the salinities calculated using the Knudsen [9] equation ($S_k = 1.805$ Cl $+ 0.03$). The differences between the specific conductivities calculated with polynomial 15 (χ_{Poisson}) and those of Thomas (χ_{Thomas}) or Reeburgh (χ_{Reeburgh}) shown in Fig. 6 as a function of salinity and in Fig. 7 as a function of temperature, call for some comments. Among all the measurements carried out by Thomas, only those made at 5°C are higher than ours; this suggests that the thermometer he used at 5°C had been badly standardized. The very great deviations obtained at 39.744‰ are due to the fact that Thomas carried out only two measurements on seawaters of salinity above 35‰. However, even at 25°C—the temperature at which those two measurements were carried out—the deviation is still very great. For other values χ_{Thomas} is always less than χ_{Poisson}.

The deviation between χ_{Reeburgh} and χ_{Poisson} remains constant at a given temperature, whatever the salinity. On the other hand, for a given salinity, this deviation always increases as temperature rises.

Reeburgh also measured the specific conductances of batches P37 and P39 of standard seawater which, normalized to a chlorinity of 19.374‰ at 25°C are 0.053067 and 0.053069 $\Omega^{-1}\cdot cm^{-1}$, respectively. These values are smaller than those we have measured, although the methods used in both laboratories to obtain the standard KCl solution are very similar.

CONCLUSION

Lewis and Perkin [18] have made a clear synthesis of the problem of the definition and calculation of salinity. In particular they emphasized the fact that the present definition of salinity [19] is the mean relation between the conductivity ratio R_{15} and the chlorinity of the various seawaters used by Cox *et al.* [8]. The use of other seawater samples would have given a slightly different relationship.

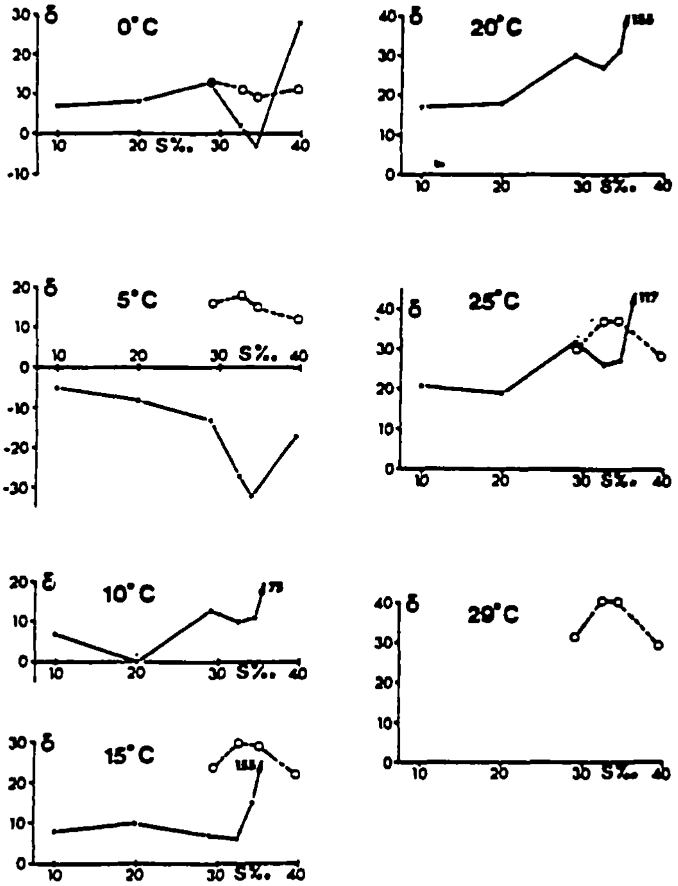

Fig. 6. Differences $\delta(10^{-6}\ \Omega^{-1}\cdot cm^{-1})$ between specific conductances calculated with polynomial 15 ($\chi_{Poisson}$) with those determinted by Thomas, χ_{Thomas} (•) or by Reeburgh, $\chi_{Reeburgh}$ (o) versus salinity at different temperatures.

One of the main features of the present work is that, the seawater we have used being strictly determined, this work can be reproduced by others [1]. Moreover, the range of salinities covered is greater than that studied by Cox. The conductivity/salinity/temperature relationships used by the various institutes in the world are often a mix of the data of Cox *et al.* (determined only for temperatures above 10°C) and of Brown and Allentoft, although these two sets of measurements are not based on seawaters with the same ionic ratio. In our work, we have extended the area of salinity and temperature studied, working only with standard seawater P75, and with a greater accuracy. The polynomials derived from experimental data can be determined in two ways. The first consists of enforcing the surface (or the curve) representing the polynomial to pass through particular curves (or points), which might deflect the surface (or curve) in their vicinity. The second consists of fitting the experimental data without taking the particular curves (or points) into account. We have chosen the first method to fit our data because it follows exactly our experimental procedure. Moreover the standard deviation is of the same order for the two methods of fitting. Additional details of our measurements will be given in another paper [19].

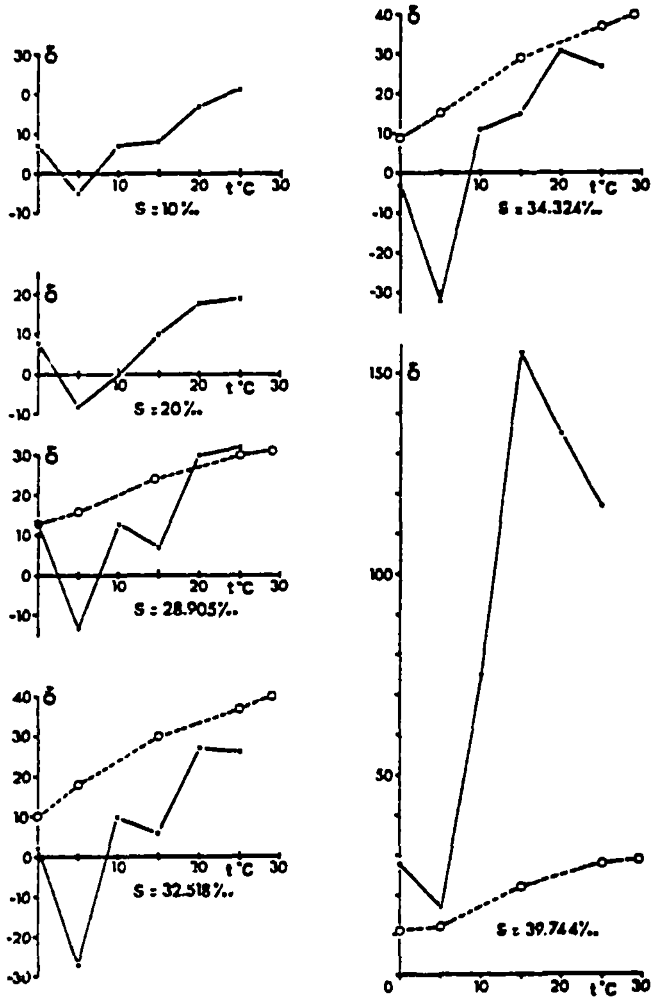

Fig. 7. Differences $\delta(10^{-6}\ \Omega^{-1}\cdot cm^{-1})$ between specific conductances calculated with polynomial 15 ($\chi_{Poisson}$) with those determined by Thomas, χ_{Thomas} (•) or by Reeburgh, $\chi_{Reeburgh}$ (o) versus temperature at different salinities.

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Electrical Conductivity of Seawater

A. L. BRADSHAW AND KARL E. SCHLEICHER

***Abstract*—Measurements of some temperature and pressure dependent relationships of the electrical conductivity of seawater at various salinities were made using four-electrode conductivity cells. At atmospheric pressure the measurements were of the effect of temperature over the range from the freezing point to about 35°C on 1) r_T (the ratio of the electrical conductivity of $35^{0}/_{00}$ seawater at temperature T to that at 15°C) and 2) R_T (the ratio of the electrical conductivity of a given seawater at temperature T to that of $35^{0}/_{00}$ seawater at the same temperature) at various salinities. The results under 1) have been combined with those of Dauphinee [1] and expressed as a fourth degree equation in temperature by Perkin and Lewis [2]. The results under 2) confirm the temperature dependence of the findings of Dauphinee [1] and of Poisson [4] for R_T as a function of salinity (weight dilution) at various temperatures. Measurements of the effect of pressure on the electrical conductivity of seawater were made for salinities of 2, 14, 22, and $35^{0}/_{00}$ over pressure and temperature ranges of 0 to 1000 bars above atmospheric pressure and the freezing point to 30°C, respectively. These results complement those of our earlier work [5] using a two-electrode conductivity cell on 31, 35, and $39^{0}/_{00}$ salinity seawaters over approximately the same pressure and temperature ranges. "Best" least squares polynomial fits in pressure and temperature to the new and to the old observed values of percentage increase in conductivity at $35^{0}/_{00}$ agree within the equivalent of $0.006^{0}/_{00}$ salinity at 1000 bars. The accuracy of the new results, which at $35^{0}/_{00}$ is probably not worse than the equivalent of $0.003^{0}/_{00}$ salinity at 1000 bars, is superior to that of the earlier ones. Perkin and Lewis [2] have fitted rational functions in P, T, R, and $\sqrt{R}$, where R is the ratio of the electrical conductivity at P, T, and salinity S to that at 0 bars, 15°C and $35^{0}/_{00}$, to the combined old and new edited data. They obtained a standard deviation of 1.3-ppm salinity for their oceanographic fit and a standard deviation of 1.3-ppm salinity for their general fit.**

BACKGROUND

THE MEASUREMENTS presented here were carried out in response to recommendations of the Joint Panel of Experts for Oceanographic Tables and Standards (JPOTS) in its sixth [6] and seventh [7] reports. In these reports this panel emphasized the need for an internationally accepted procedure for calculating the "salinity" of seawater from *in-situ* measurements of electrical conductivity, temperature, and pressure and recommended that new accurate determinations of the effect of temperature and of pressure on the electrical conductivity of seawater be carried out in order to improve upon the data base required for the formulation of such a procedure.

PART I: MEASUREMENTS AT ATMOSPHERIC PRESSURE

INTRODUCTION

Our determinations of the temperature effect on the electrical conductivity of seawater are at atmospheric pressure and consist of 1) measurements of the, electrical conductivity ratio r_T (the ratio of the electrical conductivity of $35^{0}/_{00}$ seawater at temperature T to that at 15°C) as a function of temperature and 2) measurements of the electrical conductiv-

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The authors are with Woods Hole Oceanographic Institution, Woods Hole, MA 02543.

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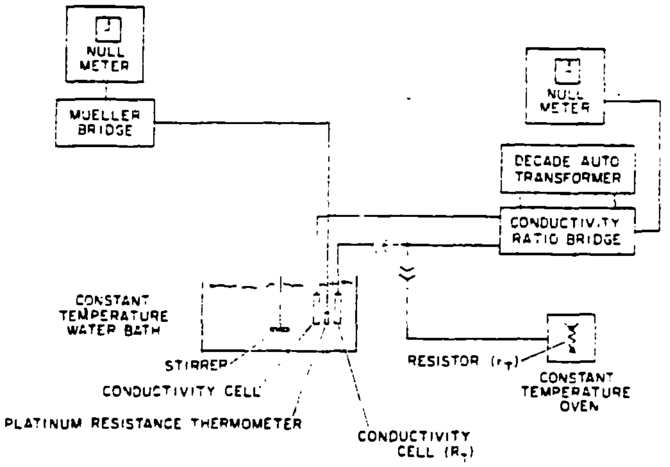

Fig. 1. Block diagram of experimental setup for measurements at atmospheric pressure. Components are: Tronac Model 400 Constant Temperature Bath with Tronac Model 40 Precision Temperature Controller; Leeds and Northrup Model 8068-B Mueller Bridge with their Model 8163-C Platinum Resistance Thermometer and Keithley Model 148 Nanovoltmeter; Neil Brown Instrument Systems Conductivity Ratio Bridge with Electro Scientific Industries Model DT 72A Decade Transformer (Dekatran) and Leeds and Northrup Model 9834 Null Meter.

ity ratio R_T (the ratio of the electrical conductivity of a given seawater at T°C to that of 35‰ seawater at the same temperature) as a function of temperature for various values of R_{15}.

APPARATUS

A block diagram of the experimental system is shown in Fig. 1. A fused quartz four-electrode conductivity cell (Fig. 2) was used in the measurements of r_T and two Pyrex four-electrode conductivity cells (Fig. 2) were used in the measurements of R_T. In both of these experiments the platinum electrodes of the cells were platinized with a very thin but fairly black coating of platinum black. In the first experiment the ratio of the cell conductance to the conductance of a 300-Ω Vishay resistor, which had four-terminal connections and which was kept at constant temperature, was measured; in the second experiment, the ratio of the conductances of the two cells was the measured quantity. A simplified schematic of the conductivity ratio bridge circuit is given in Fig. 3. The bridge was calibrated for ratio errors by interchange of resistors at a ratio of 1 and by using a resistance ladder for smaller values of the ratio. The error increases linearly from 0×10^{-6} at a ratio of 1 to 13×10^{-6} as the ratio approaches 0. The errors in the Dekatran ratio transformer (given in its certificate of calibration) are insignificant. The voltage leads to each conductivity cell consisted of two 2-foot lengths of 14 pF/ft shielded coaxial cable and the current leads were made from a similar length of the same cable with the shield serving as one of the current paths; the shields of both the voltage and current leads were grounded, as was also the bath water. The temperature of the water bath stayed constant at each measurement point to within ±0.3 m°C and was measured with the resistance element of the platinum resistance thermometer close to and at approximately the same depth as the bottom of the measuring section of the cell (s). The measuring arm of the Mueller bridge was calibrated for deviations from linearity by four-terminal measurements using a Guildline Current Comparator Resistance Bridge (Model 9975) and a Guildline four-terminal resistor held at constant temperature in an air oven. The platinum

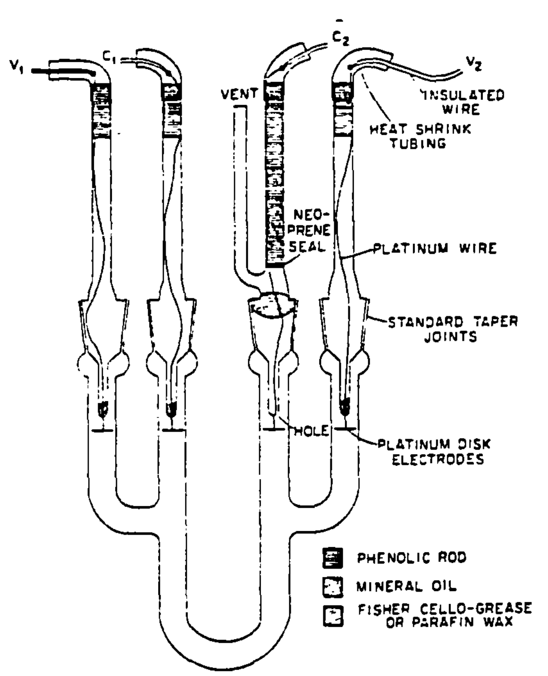

Fig. 2. Conductivity cells used for atmospheric pressure measurements. The same cell design was used in both the r_T and R_T measurements. The path lengths from the voltage and current electrode to the junction of the voltage and current arms on each side of the cell was chosen great enough to make the cell constant independent of the electrical conductivity of the sample. In the case of the r_T cells Pyrex joints were joined to the remaining fused-quartz section of the cell (measuring section) by graded seals. The R_T cells were made entirely of Pyrex and faced each other in parallel planes about 10 cm apart. The cell volume is ~20 cm^3 and the cell constants are ~27 cm^{-1} (r_T) and ~31 cm^{-1} (R_T).

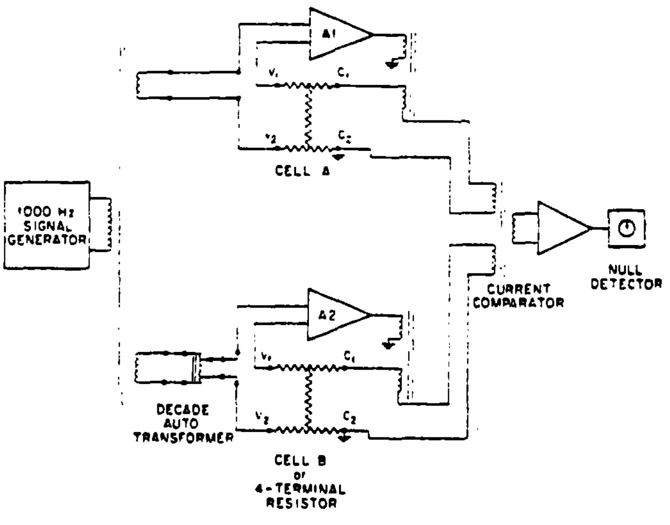

Fig. 3. Simplified schematic of conductivity ratio bridge circuit. $A1$ and $A2$ are very-high-gain operational amplifiers; V_1, V_2 and C_1, C_2 are voltage and current terminals. The voltage across $C_1 - C_2$ is about 0.2 V. The bridge is balanced by adjusting the voltage input from the decade auto transformer (Dekatran).

resistance thermometer had been recalibrated by the National Bureau of Standards before conductivity measurements were begun and its resistance at the triple point of water was determined periodically after that time.

PROCEDURE

A. Variation of the Conductivity Ratio r_T with Temperature

Three runs were made on P73 (Cl = 19.375‰) standard seawater. Before each run the fused quartz conductivity cell (see Fig. 2) was cleaned with detergent, rinsed first with distilled water and then with acetone, and finally dried with dry nitrogen. The vented electrode plug was cleaned on the inside and outside with distilled water and the inside was rinsed with acetone and dried with dry nitrogen. The sealed electrode plugs were rinsed with distilled water and dried with tissue. The ground inner joint sections of the plugs were greased with Fisher Celloseal grease and the three sealed electrode plugs were loosely inserted into the corresponding outer joints in the cell arms. The cell was then filled through the vented electrode arm from a standard seawater ampoule via a length of rubber tubing which was connected to a short section of glass tubing with a rubber stopper on it. In doing this, each of the three electrode plugs was lifted in sequence for flushing of the corresponding cell arm until about one-half or more of the ampoule of seawater had been used up. The sealed electrode plugs were then rotated into the joints. The level of sample in the filling arm was lowered to a predetermined level using a syringe and tubing, and the vented electrode plug was rotated into place. A 5- to 7-mm-thick layer of light pure mineral oil (Exxon Isopar-M) was then placed on the seawater surface with a syringe and tubing. The pH of a sample of the standard seawater was measured. In each of the three runs measurements were made following the temperature sequence 15, 10, 5, 0, freezing point, 15, 20, 25, 30, 35, and 15°C. At each point averages of temperatures and of conductance ratios were taken after they became stable, and the dc resistance of the cell to bath water, when the electrode leads were disconnected, was checked. This resistance was always greater than 1000 MΩ, which in the case of the cell used would produce a shunting error less than the equivalent of 0.00003‰ salinity. The conductance ratios were corrected for the thermal expansion of the conductivity cell, using the function for the mean volume coefficient of thermal expansion of fused quartz given in Bradshaw and Schleicher [14]. This correction amounts to about -0.4×10^{-6} $(°C)^{-1}$ and is equivalent to less than 0.0004‰ salinity in the temperature interval on either side of 15°C.

B. Variation of the Conductivity Ratio R_T with Temperature

The procedure for cleaning and filling each of the two Pyrex conductivity cells used in these experiments was identical to that described in Section A. The cell constants of the cells were determined at 15°C using P75 (Cl = 19.374‰) standard seawater, which was transferred to the cells directly from the ampoules. All seawater samples used for the runs were prepared by dilution of P75 standard seawater or of ~44‰ salinity seawater which had been prepared from the same source by slow evaporation at 70°C. Double-distilled water having an electrical conductivity of 1×10^{-6} $(\Omega\cdot\text{cm})^{-1}$ was used in the dilutions and the sample seawater was equilibrated with laboratory air. Both the sample seawater and the P75 seawater used in the 35‰ cell were degassed by partially filling a vacuum flask with the seawater, evacuating the air space in the flask, and then closing the vacuum inlet and stirring the seawater for 1 to 2 h. This process raised the salinity of the P75 seawater from 35.000 to a maximum of 35.013‰. The effect of the slight deviation from 35.000‰ on the temperature variation of R_T is negligible. The pH of both seawaters was measured. All runs followed the temperature sequence 15, 10, 5, 0, freezing point of the lower salinity seawater, 15, 20, 25, 30, 36, and 15°C. Measurements of the conductance ratio, the temperature, and the dc resistance from each cell to the bath water were made at each point, as in Section A.

Included in the runs was one using the same sample (degassed) of P75 seawater in each cell. This run was made in order to determine directly the cell constant ratio, and its temperature dependence, if any. Analysis of the results indicated a linear regression of conductance ratio on temperature: the cell constant ratio (the reciprocal of the conductance ratio) was about 0.98 and its temperature coefficient was 0.42×10^{-6} $(°C)^{-1}$ with an estimated standard error of 0.13×10^{-6} $(°C)^{-1}$. The cause(s) of this slight variation of conductance ratio with temperature are unknown. The magnitude of the variation is about 10 percent of the linear thermal expansion of Pyrex glass, but it is equivalent to not more than 0.0003‰ salinity in $R_{15} - R_T$ over the temperature ranges of the measurements. The measured conductance ratios in all of the runs were divided by the conductance ratios given by the above regression formula at the corresponding temperatures, in order to correct them for the inequalities in cell constants and cell temperature coefficients.

RESULTS

"Best" polynomial fits for the regression of conductance ratio on temperature for all the runs described in A and B under Procedure were computed. The degree of the polynomial was found in each case by testing the coefficient of the highest power of polynomials of successively higher degree for significance at the 5-percent level using the F test. The conductance ratio at 15°C was then estimated from the polynomial.

In the case of the runs for the effect of temperature on the conductivity of standard seawater, the estimated conductance ratio at 15°C was divided into the measured conductance ratios to give the observed values for the ratio r_T. These values with the observed temperatures are presented in Table I, along with an estimate of the standard error for a single observation, which was calculated from the residuals and their number of degrees of freedom.

The observed values of R_T and temperature T for each R_{15} (estimated from the polynomial fit) are given in Table II, along with the degree of the polynomial fit and the estimated standard error for a single observation.

TABLE I

OBSERVED VALUES OF THE ELECTRICAL CONDUCTIVITY RATIO r_T AS A FUNCTION OF TEMPERATURE*

Run 1		Run 2		Run 3	
pH = ?		pH(25°C) = 8.2		pH(25°C) = 8.0	
T_{68}°C	r_T	T_{68}°C	r_T	T_{68}°C	r_T
15.0159	1.000358	15.0162	1.000366	15.0142	1.000307
10.0018	0.887567	10.0056	0.887648	10.0050	0.887625
4.9930	0.779414	4.9920	0.779398	5.0069	0.779713
-0.0917	0.674761	-0.1075	0.674450	-0.0886	0.674831
-1.8045	0.640776	-1.8654	0.639580	-1.9031	0.638841
15.0157	1.000341	15.0157	1.000356	15.0142	1.000316
15.0162	1.000364	15.0163	1.000375	15.0141	1.000318
20.0126	1.116784	20.0177	1.116921	20.0039	1.116592
25.0054	1.236675	25.0155	1.236921	25.0062	1.236696
30.0087	1.359900	30.0382	1.3[illegible]7	30.0193	1.360166
36.0341	1.511805	36.0311	1.5[illegible]733	36.0227	1.511521
15.0163	1.000414	15.0159	1.000375	15.0135	1.000347

Degree of polynomial fit (N) and the standard error for a single observation (σ), estimated from the residuals to this fit:

Run 1	Run 2	Run 3
N = 4	N = 4	N = 4
$\sigma = 18 \times 10^{-6}$	$\sigma = 6 \times 10^{-6}$	$\sigma = 18 \times 10^{-6}$

* The measurements were made on standard seawater P 73 (Labeled chlorinity = 19.375 $^{o}/oo$) and are presented in chronological order. The error caused by the deviation of the salinity of this seawater from 35$^{o}/oo$ is negligible.

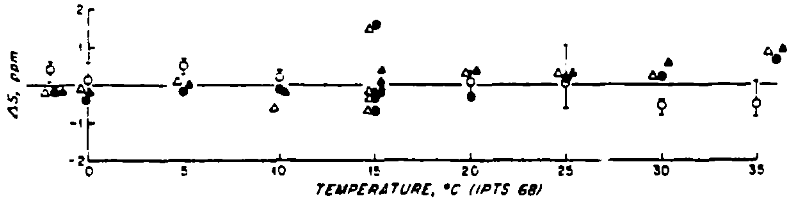

Fig. 4. Residuals of r_T results from Perkin and Lewis fit expressed in equivalent salinity units. Present results: ●, Run 1; ▲, Run 2; △, Run 3. Dauphinee: Φ, average value and range of values.

ACCURACY OF TEMPERATURE EFFECT RESULTS

The inaccuracy in the observed values for r_T is believed not to be greater than the equivalent of $0.002^{o}/_{oo}$ salinity. This is based on an estimated maximum systematic error of 0.001°C in the temperature difference $T - 0$°C and a standard error for a single observation equal to $0.0003^{o}/_{oo}$; the latter was estimated from the average of the variances at all of the temperature points (using Fig. 4). The two uppermost points at 15°C in Fig. 4 were the final ones from two different runs; their deviations from the other points at this temperature suggest additional systematic errors in the cycle going from 15°C to 36°C and back to 15°C in these two runs. From the good agreement of the points in going up to 36°C, it seems probable that the cause(s) of these occur during the second half of the cycle.

The uncertainty in the observed values of R_T is estimated to be not worse than 2×10^{-5} which is equivalent to about $0.001^{o}/_{oo}$ in salinity. This is based on negligible systematic error and a standard error of 6×10^{-6} for a single observation. The latter value was calculated from the mean value of the variances of the observed quantity for the nine runs; each of these variances was estimated from the residuals for the fit using the appropriate number of degrees of freedom.

TABLE II
OBSERVED VALUES OF THE ELECTRICAL CONDUCTIVITY RATIO R_T AS A FUNCTION OF TEMPERATURE FOR VARIOUS VALUES OF R_{15}*

R_{15} = 0.072211		R_{15} = 0.200693		R_{15} = 0.496689	
T_{68}	R_T	T_{68}	R_T	T_{68}	R_T
15.0024	0.072208	15.0040	0.200693	15.0081	0.496689
10.0055	0.071883	10.0064	0.199970	10.0105	0.495690
5.0014	0.071481	5.0021	0.199112	5.0055	0.494486
-0.0063	0.071005	0.0147	0.198070	0.0074	0.493002
15.0019	0.072210	-0.2585	0.198005	-0.7779	0.492736
20.0075	0.072506	15.0030	0.200692	15.0070	0.496688
25.0022	0.072778	20.0087	0.201319	20.0136	0.497541
30.0002	0.073021	25.0029	0.201869	25.0084	0.498283
35.0102	0.073242	30.0011	0.202366	30.0072	0.498943
15.0030	0.072212	35.0097	0.202826	35.0162	0.499538
		15.0032	0.200692	15.0075	0.496692

R_{15} = 0.767632		R_{15} = 0.900243		R_{15} = 1.000000	
T_{68}	R_T	T_{68}	R_T	T_{68}	R_T
15.0058	0.767619	15.0039	0.900241	15.0151	1.000007
10.0090	0.766964	10.0061	0.899923	15.0152	1.000006
5.0048	0.766166	5.0020	0.899535	10.0052	1.000008
-0.0038	0.765174	0.0148	0.899054	4.9828	1.000000
-1.3056	0.764873	-1.5742	0.898870	-0.0374	0.999995
15.0051	0.767625	15.0026	0.900242	-1.0998	0.999999
20.0109	0.768182	20.0090	0.900513	15.0307	0.999993
25.0059	0.768666	25.0034	0.900746	15.0276	0.999997
30.0036	0.769094	30.0012	0.900954	20.0088	0.999995
35.0129	0.769477	35.0101	0.901136	25.0035	0.999995
15.0084	0.767648	15.0038	0.900250	30.0022	0.999999
				36.0431	1.000003
				15.0299	1.000001

R_{15} = 1.093509		R_{15} = 1.171246		R_{15} = 1.228605	
T_{68}	R_T	T_{68}	R_T	T_{68}	R_T
15.0010	1.093500	15.0034	1.171245	15.0035	1.228598
10.0042	1.093859	10.0060	1.171917	10.0061	1.229536
4.9989	1.094286	5.0020	1.172735	5.0015	1.230679
0.0113	1.094828	0.0144	1.173763	0.0143	1.232089
-1.8900	1.095065	-1.8869	1.174221	-1.6640	1.232636
15.0012	1.093516	15.0023	1.171248	-1.8882	1.232729
20.0078	1.093226	20.0082	1.170683	15.0025	1.228611
25.0029	1.092972	25.0026	1.170194	20.0082	1.227820
30.0010	1.092750	30.0070	1.169765	25.0023	1.227147
35.0092	1.092550	35.0092	1.169390	30.0005	1.226560
15.0023	1.093515	15.0032	1.171241	35.0089	1.226038
				15.0032	1.228604

TABLE II (*continued*)

The pH values of the seawater samples, and the degree of the polynomial fit to the data (N) and the standard error for a single observation (σ), estimated from the residuals to this fit are given below:

	35 ‰ Seawater		R_{15} Seawater			
R_{15}	pH	@ T°C	pH	@ T°C	N	$\sigma \times 10^6$
0.072211	7.8	25	7.3	27	4	4
0.200693	7.8	28	7.7	28	5	1
0.496689	7.8	28	7.9	28	4	2
0.767632	7.8	28	8.0	29	3	11
0.900243	7.9	28	8.1	28	4	3
1.000000	7.8	28	7.8	28	1	5
1.093509	7.9	26	8.3	26	3	7
1.171246	?	-	8.3	29	4	2
1.228605	7.8	28	8.5	26	4	6

* At each R_{15} the values are given in chronological order. Source of seawater was Standard Seawater P 75.

COMPARISONS

Perkin and Lewis [2] have combined the results of Dauphinee [1] for r_T with ours and fitted the resulting set of observations with a fourth degree polynomial in temperature. The residuals of both sets of results from this fit are shown in Fig. 4. A comparison of the data from some earlier investigations of the temperature effect on the electrical conductivity of standard seawater [8], [9] with the above fit is shown in Fig. 5.

The quantity $\Delta = R_{15} - R_T$ was calculated for each of the observed values of R_T and T in Table II and compared with the corresponding values given by the fit $S = f(T, R_T)$ of Perkin and Lewis [2] to the combined data of Dauphinee [1] and Poisson [4] for R_T as a function of weight dilution salinity at various temperatures. The differences are presented in Fig. 6. With the possible exception of the high-temperature low-salinity corner of the measurement region they confirm the above results of Dauphinee and of Poisson. Cox *et al.* [10, Table 3) and Brown and Allentoft [9, Table 23] also measured the effect of temperature on R_T; similar comparisons of their observed values for Δ with those calculated from $S = f(T, R_T)$ are shown in Figs. 7 and 8.

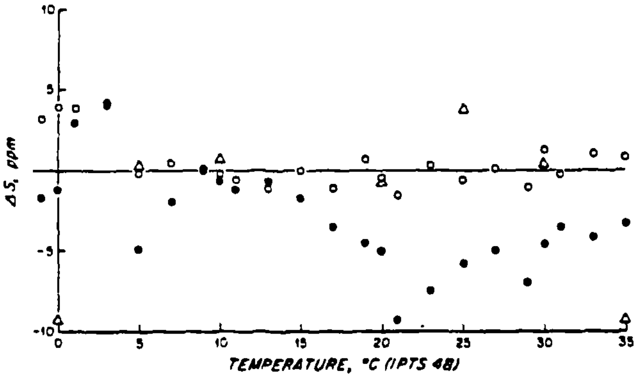

Fig. 5. Comparison of results of some earlier investigators for r_T with Perkin and Lewis equation. Theirs minus P & L expressed in equivalent salinity units. Reeburgh: ○, P37 Standard Seawater (Cl = 19.369‰); ●, P39 Standard Seawater (CL = 19.372‰). Brown and Allentoft: Δ, P41 Standard Seawater (Cl = 19.373‰). The points corresponding to $r_T = 1$ at 15°C ($\Delta S = 0$) are not shown. The two points of Reeburgh shown at 15°C correspond to repeated measurements at the conclusion of each of his two runs.

PART II: MEASUREMENTS OF THE EFFECT OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF SEAWATER

INTRODUCTION

Earlier measurements of the effect of pressure on the electrical conductivity of seawater include those of Hamon [11], Horne and Frysinger [12], and Bradshaw and Schleicher [5]. Hamon's measurements are for a single salinity (35.6‰) and for a pressure increment of 100 bars over a temperature range of 0 to 20°C; their accuracy is equivalent to about 0.02‰ salinity or better. Horne and Frysinger's data is for almost all of the oceanographic region of temperature, pressure, and salinity, but suffers from inaccuracies that are at least as large as the equivalent of 1‰ salinity [5]. Bradshaw and Schleicher's data is for the region defined by 0 to 25°C in temperature, 0 to 1000 bars in applied pressure and 31 to 39‰ in salinity. The claimed accuracy of this data is equivalent to 0.01‰ salinity or better. In support of this accuracy claim, Brown [13] found agreement within ±0.003‰ in about 75 percent of the cases down to 4500 m with his CTD, using bottle sample salinities. The measurements of the effect of pressure on the electrical conductivity of seawater presented here extend the salinity range of these earlier measurements down to about 2‰ salinity, in order to include Baltic, Black

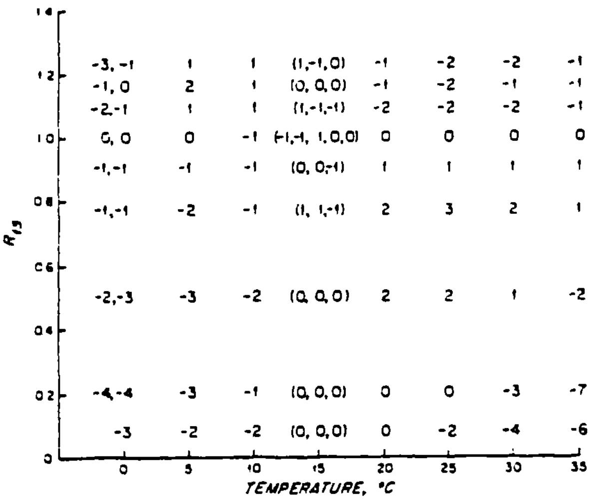

Fig. 6. Comparison of present results for $\Delta = R_{15} - R_T$ with those from Perkin and Lewis fit to the results of Dauphinee and of Poisson for R_T as a function of weight dilution salinity and temperature. Present minus P & L. Unit is $10^{-5}\Delta$.

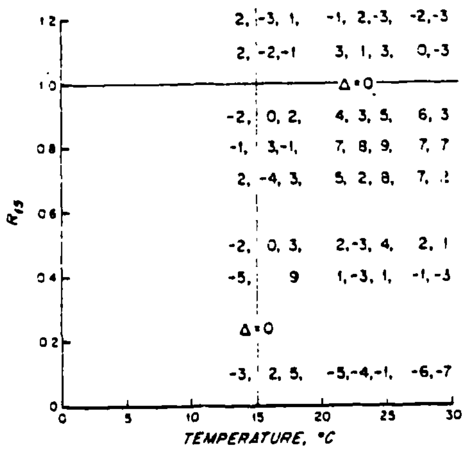

Fig. 7. Comparison of the results of Cox *et al.* for Δ with those from Perkin and Lewis fit. Cox *et al.* minus P & L. Unit is $10^{-5}\Delta$.

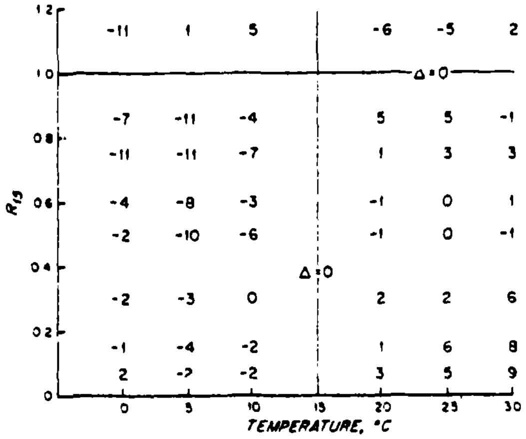

Fig. 8. Comparison of the results of Brown and Allentoft for Δ with those from Perkin and Lewis fit. B & A minus P & L. Unit is $10^{-5}\Delta$.

Sea, and low salinity surface seawaters; to check consistency with our earlier results, data at 35‰ salinity was also taken.

APPARATUS

A block diagram of the experimental system is shown in Fig. 9. The water bath, except for minor modifications which improved the temperature control to about ±0.001°C, was the same one used in our seawater thermal expansion measurements [14]. Also, the pressure vessel was the same one used in our earlier work on the pressure effect on the electrical conductivity of seawater [5]. The pressure vessel is made of aluminum alloy and has six electrical leadthroughs, four of which were used for the four-electrode Pyrex conductivity cell (a two-electrode cell was used in our earlier measurements) and one for the protected thermistor (the return path was through the pressure vessel). The conductivity cell (Fig. 10) was held by plastic tubing clamps to a lucite frame which was suspended from the bottom of the pressure vessel plug. Electrical connections from the leadthroughs to the cell electrode leads were made with spring loaded clamps. The electrodes were platinized (see Part I-Apparatus).

The pressure-protected thermistor was at the same level as the bottom *U* of the conductivity cell. This thermistor was enclosed in a cylindrical brass pressure case which had been partially filled with light mineral oil (Isopar–M) for thermal conduction. The thermistor resistance formed one arm of a dc Wheatstone bridge which consisted of Vishay resistors and a precision voltage divider (ESI DP1311 Dekapot) in the ratio arms for balancing the bridge. This system was calibrated against a platinum resistance thermometer[1] in a Tronac water bath at 5°C intervals from 0 to 30°C. The residuals from the calibration, which assumed that the Steinhard-Hart [16] temperature-thermistor resistance function was valid, gave a standard error of 0.2 m°C for a single observation. The self-heating temperature rise of the thermistor was 0.4 to 0.5 m°C.

The light mineral oil (Isopar-M) in the pressure vessel was stirred by a four-bladed fan at the bottom; this fan was driven by a magnet attached to the bath stirrer shaft.[2] Because an oil heavier than the light mineral oil in the pressure vessel was used in the piston gage, a *U*-type separator containing distilled water in the bottom of the *U* was placed between the two oils. During the measurement runs the system was brought to the approximate pressure using the hand-operated pump and then the valve between the system and the piston gage was opened.

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[1] Both the platinum resistance thermometer and the resistance measuring bridge (Guildline Current Comparator Resistance Bridge) used in this calibration were different from those which were used in the experiments in Part I and also to monitor the water bath temperature in the experiments in Part II. However, the differences between temperatures given by the two combinations over the temperature range of the measurements was not more than 0.7 m°C. The effect of these differences on the results in this section is insignificant and was neglected.

[2] From Bridgman's data on the pressure effect on the viscosity of kerosene [15] it was estimated that the viscosity of the mineral oil used at 1000 bars should be less than that of SAE 10 oil at atmospheric pressure. Because the fan stirred SAE 10 oil adequately at atmospheric pressure, it was assumed that this was true in the case of Isopar-M at 1000 bars.

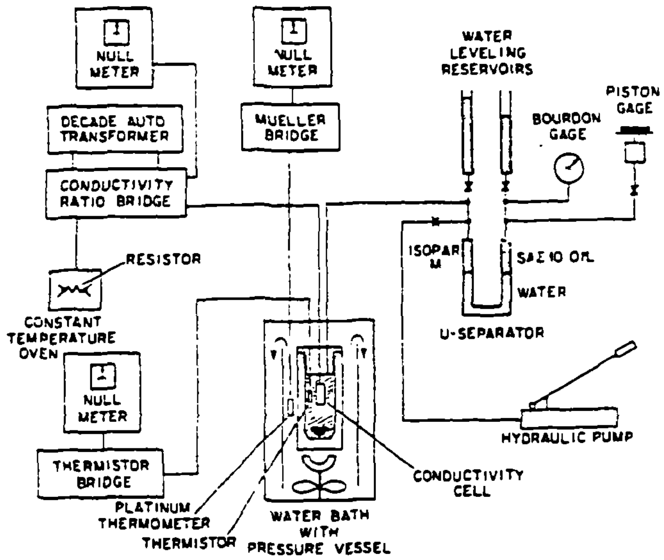

Fig. 9. Block diagram of experimental system for the measurement of the effect of pressure on the electrical conductivity of seawater. X is the symbol for a valve.

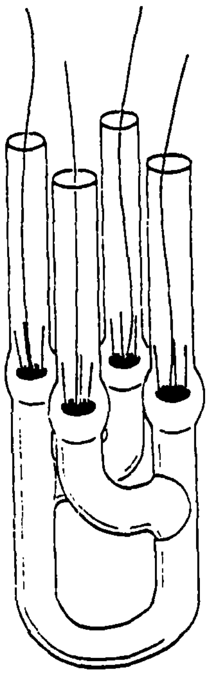

Fig. 10. Sketch of conductivity cell used for the measurement of the effect of pressure on the electrical conductivity of seawater. Its volume and cell constant are ~20 cm^3 and ~24 cm^{-1}.

The Aminco piston gage (Model 47-12218) is of the simple cylinder type. Its indicated pressure includes an error due to the change of the effective area of the piston with pressure. The correction for this effect was found by comparison with a Harwood controlled clearance free piston gage, Model DWT-1000-20000 psi, which had been calibrated using the same oil as the Aminco gage. The accuracy of our corrected pressure readings (see Part II Workup of Data) is estimated to lie between 0.01 and 0.02 percent of the pressure at 1000 bars.

EXPERIMENTAL PROCEDURE

Before each cell constant determination or set of pressure effect measurements the conductivity cell was cleaned by first rinsing with water and acetone, then soaking in a strong detergent solution, and, finally, after rinsing with distilled water, drying with acetone and dry nitrogen. The cell was then filled nearly to the top of each cell arm with the seawater sample and 1 to 2 cm of Isopar-M was placed on the seawater surfaces to prevent evaporation.

The cell constant was determined by measurements on samples from three ampoules of P75 standard seawater in a Tronac water bath at 15°C. This value of the cell constant agreed within 0.006 percent with the value determined (using P75 standard seawater) with the cell in the oil-filled pressure vessel.

The set of pressure effect measurements at each salinity was run on a single sample of seawater. All of the seawater samples were prepared by dilution of P75 standard seawater in the manner described in Part I, Section B. The procedure at each salinity was to begin measurements at one of the scheduled temperatures and at 0 piston gage pressure; then to make measurements at three ascending pressures only slightly above 0 (~6, ~9, and ~16 bars), in order to check for the absence of gas bubbles in the measuring section of the cell (by linear extrapolation to zero gage pressure); and finally to continue from 200 bars to 1000 bars at 200 bar intervals of pressure, and then to return to 0 gage pressure in order to check for cell drift. At each pressure conductance ratio and thermistor temperature readings were taken until they became constant with time. At zero gage pressure and occasionally at higher pressures platinum thermometer readings of the water bath temperature were taken and averaged. Readings of piston gage temperature and barometric pressure were recorded.

WORKUP OF DATA

Piston gage readings were corrected for the difference between local and standard gravitational acceleration, air buoyancy of the weights, the temperature effect on the gage piston and cylinder, the pressure effect on the gage piston and cylinder (see Apparatus), and the fluid head between the gage piston and the sample. The variation in barometric pressure during the runs was small enough to be neglected.

In each run on 35‰ salinity seawater thermistor temperatures were corrected (by linear interpolation with time) for thermistor drift using the platinum thermometer temperatures of the water bath taken at the beginning and end of the run. In one of these runs (at −1.85°C) the drift was 0.7 m°C; in the remainder it was not more than 0.2 m°C. In the runs at lower salinities the thermistor drift was not more than 0.8 m°C and because of the reduced effect of temperature on the final results at these salinities was neglected; the errors introduced into the pressure effect data in consequence were not more than the equivalent of 0.2 ppm in salinity.[3]

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[3] Part or all of the assumed thermistor drift in all of the runs could be due to changing temperature gradients in the water bath and inside the pressure vessel.

TABLE III
OBSERVED VALUES FOR THE PERCENTAGE INCREASE IN THE ELECTRICAL CONDUCTIVITY OF SEAWATER AT VARIOUS TEMPERATURES AND SALINITIES*

S = 35.009 $^{o}/oo$ (R_{15} = 1.000231), pH (28°C) = 8.0

Pressure (bars above atmospheric)	Temperature, t_{68} (°C)						
	-1.85	4.25	10	15	20	25	30
0.1	0.000	0.000	0.001	0.001	0.001	0.000	0.000
5.9	0.100	0.083	0.070	0.061	0.054	0.048	0.042
9.3	0.160	0.131	0.111	0.096	0.085	0.076	0.067
16.2	0.276	0.227	0.193	0.167	0.148	0.131	0.116
199.8	3.187	2.634	2.231	1.947	1.713	1.516	1.349
399.6	5.935	4.912	4.167	3.641	3.204	2.837	2.524
599.4	8.269	6.860	5.826	5.095	4.487	3.973	3.538
799.1	10.221	8.494	7.225	6.325	5.573	4.938	4.397
998.8	11.822	9.845	8.385	7.346	6.477	5.740	5.113
0.1	0.001	0.000	0.001	0.000	0.000	0.000	0.000

S = 22.065 $^{o}/oo$ (R_{15} = 0.659615), pH (25°C) = 8.1

Pressure (bars above atmospheric)	Temperature, t_{68} (°C)						
	-1	5	10	15	20	25	30
0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001
5.9	0.106	0.088	0.075	0.066	0.058	0.051	0.045
9.3	0.168	0.139	0.119	0.104	0.091	0.080	0.071
12.8	--	--	--	--	0.124	--	--
16.2	0.291	0.240	0.207	0.180	--	0.139	0.125
199.8	3.361	2.784	2.398	2.084	1.826	1.609	1.426
399.6	6.294	5.200	4.486	3.901	3.418	3.013	2.670
599.4	8.784	7.271	6.278	5.465	4.791	4.224	3.744
799.1	10.876	9.018	7.796	6.792	5.958	5.254	4.658
998.8	12.599	10.467	9.059	7.899	6.933	6.116	5.420
0.1	0.000	0.001	0.000	-0.001	0.000	0.000	0.001

S = 35.000 $^{o}/oo$ (R_{15} = 1.000000), pH (25°C) = 7.7

Pressure (bars above atmospheric)	Temperature, t_{68} (°C)
	15
0.1	0.001
5.9	0.061
9.3	0.096
16.2	0.168
998.8	7.350
0.1	0.000

TABLE III (*continued*)

S = 14.051 ‰ (R_{15} = 0.436718), pH (25°C) = 7.9

Pressure (bars above atmospheric)	Temperature, t_{68} (°C) -0.5	5	10	15	20	25	30
0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001
5.9	0.109	0.092	0.079	0.068	0.059	0.050	0.046
9.3	0.173	0.145	0.124	0.108	0.094	0.080	0.073
16.2	0.300	0.251	0.215	0.186	0.162	0.140	0.126
199.8	3.486	2.912	2.499	2.164	1.688	1.655	1.464
399.6	6.507	5.441	4.674	4.050	3.536	3.102	2.742
599.4	9.085	7.608	6.543	5.675	4.956	4.351	3.845
799.1	11.255	9.440	8.127	7.054	6.164	5.413	4.784
998.8	13.050	10.961	9.447	8.206	7.174	6.302	5.566
0.1	0.000	0.001	0.000	0.000	0.000	-0.003	0.002

S = 2.034 ‰ (R_{15} = 0.072133), pH (21°C) = 7.3

Pressure (bars above atmospheric)	Temperature, t_{68} (°C) 0	5	10	15	20	25	30
0.1	0.001	0.001	0.001	0.000	0.001	0.000	0.000
5.9	0.116	0.098	0.083	0.072	0.060	0.054	0.047
9.3	0.183	0.154	0.132	0.115	0.097	0.086	0.075
16.2	0.317	0.267	0.227	0.197	0.167	0.147	0.129
199.8	3.644	3.062	2.603	2.232	1.923	1.671	1.456
399.6	6.792	5.712	4.858	4.166	3.593	3.119	2.717
599.4	9.471	7.976	6.789	5.825	5.025	4.362	3.797
799.1	11.717	9.881	8.416	7.226	6.234	5.411	4.708
998.8	13.565	11.456	9.765	8.387	7.238	6.279	5.459
0.1	0.001	0.002	0.002	0.006	0.002	0.005	0.005

* Source of seawater was Standard Seawater P 75. The measurements were made in chronological order with respect to pressure and salinity.

All of the actual pressures in the runs were within 0.05 bars of the reported values (Table III), except in nine instances in the case of the 14‰ and 2‰ runs where the differences were between 0.06 and 0.10 bars. No corrections have been made for these differences between the observed and reported pressures; such corrections would be equivalent to less than 0.3-ppm salinity. All of the actual temperatures were within 0.02°C of the reported values with the exception of the 0°C data in the 2‰ seawater runs where the maximum difference was 0.09°C. The conductance ratio data was adjusted to the reported values of the temperature using a Lagrange-formula fitted through all the points at a given pressure. At each of the adjusted temperatures in all of the runs the 0 applied pressure conductance ratio value was determined by a linear regression of conductance ratio on pressure through the first four low pressure points taken. The fits were linear to within the precision of the data. The observed values for the percentage increase in electrical conductance of seawater were then calculated after making a correction for the decrease in the conductivity cell constant with pressure due to the compressibility of Pyrex glass. A value of 0.00306/ 1000 bars for the volume compressibility of Pyrex [5] was used in making the correction. The results are presented in Table III. The final values at 0.1 bar in Table III have been included to indicate the magnitude of the drift in cell conductance. The salinities given in the table were computed from the values of R_{15} using the Dauphinee-Poisson equation for $S = f(R_{15})$ [2].

The value for the percentage increase in electrical conductivity in Table III are listed chronologically with respect to salinity and pressure. After completing the set of measurements at 22‰ salinity the conductivity cell was broken. In order to check the reproducibility of the effect of pressure on

TABLE IV
DIFFERENCES BETWEEN EARLIER [5] AND PRESENT RESULTS FOR PERCENTAGE INCREASE IN ELECTRICAL CONDUCTIVITY OF SEAWATER AT 35‰ SALINITY AS ESTIMATED FROM POLYNOMIAL FITS TO THE DATA (EARLIER MINUS PRESENT). (THE ESTIMATED STANDARD ERROR OF THE DIFFERENCE IS GIVEN IN PARENTHESES.)

Applied Pressure, bars	Temperature, °C 0	5	10	15	20	25
200	0.001(0.002)	0.002(0.001)	-0.001(0.001)	0.002(0.001)	0.003(0.001)	-0.002(0.002)
400	0.005(0.002)	0.005(0.001)	0.001(0.001)	0.002(0.001)	0.005(0.001)	-0.001(0.002)
600	0.009(0.002)	0.008(0.001)	0.001(0.001)	0.001(0.001)	0.006(0.001)	0.001(0.002)
800	0.011(0.002)	0.012(0.001)	0.003(0.001)	0.002(0.001)	0.007(0.001)	0.004(0.002)
1000	0.010(0.002)	0.017(0.002)	0.008(0.002)	0.007(0.002)	0.012(0.002)	0.013(0.002)

the cell constant of the new conductivity cell, a run was made on 35‰ salinity seawater at 15°C before proceeding with the remainder of the measurements. The difference in the pressure effects on electrical conductivity at 1000 bars measured with the two cells is equivalent to 0.002‰ salinity. This is considered to be close to the uncertainty of the measurements.

ACCURACY OF PRESSURE EFFECT RESULTS

The maximum uncertainty in the observed values occurs at 35‰ salinity, where it is believed to be not more than the equivalent of 0.003‰ salinity. This is based on a maximum possible systematic error equivalent to 0.0014‰ salinity and a standard error for a single observation equivalent to 0.0003‰ salinity.

The systematic error was taken as the sum of the effects at 1000 bars and −1.85°C due to errors of 1) 1 percent in the value used for the compressibility of Pyrex [5], 2) 0.002‰ in the salinity value, 3) 0.02 percent of the reported pressure, and 4) 0.003°C in the temperature value. The value used for the temperature error is the maximum difference between the thermistor temperature inside the pressure vessel and the platinum thermometer temperature in the water bath. It occurred only at the higher end of the temperature range and appeared to be stable with pressure.

The standard error was estimated from the residuals for a "best" polynomial fit to the results at 35‰ (see following section) using the appropriate number of degrees of freedom.

COMPARISON WITH OUR EARLIER RESULTS AT 35‰ SALINITY

Adjustments must be made to our earlier results before they can be compared with the ones presented here. The IPTS-48 temperatures must be converted to the IPTS-68 scale and the pressures must be corrected for the effect of pressure on the effective area of the piston of the piston gage. The piston-cylinder design of the Aminco piston gage used in the previous work, except for minor differences in the dimensions of the piston, was exactly the same as that of the Aminco balance used in the present work. A comparison of the old and the new gages made at ~1000 bars many years ago showed agreement within 0.5 psi,which was the smallest balance weight used on the old gage; this is equivalent to 0.03 bars. The pressure correction is thus assumed to be the same as that found for the new gage and so the formula for correcting the pressures of the previous work is given by

$$P_{\mathrm{new}} = P_{\mathrm{old}}\,(0.999901 - 2.57 \times 10^{-7}\,P_{\mathrm{old}}),$$

where P is in bars, applied pressure.

The salinities of the earlier data were measured on a Woods Hole Oceanographic Institution conductance salinometer operating at 15°C. The salinometer had been calibrated by weight chlorinity dilution of seawater which had been concentrated to ~39‰ salinity by slow evaporation and application of the equation $S = 0.03 + 1.805\ \mathrm{Cl}$ to convert chlorinities to salinities. The latter equation is the empirical relationship of Forch *et al.* [17], which was used at the time for defining salinity. Use of this equation instead of $S = 1.80655\ \mathrm{Cl}$, which is consistent with the weight dilution scale of the present measurements, introduces errors at 31 and 39‰ of 0.003 and −0.003‰, respectively. However, these salinity errors contribute errors in the effect of pressure on electrical conductance which are equivalent to at most 0.0001‰ salinity and, furthermore, they are small compared with the estimated uncertainty of 0.03‰ in the salinity determinations of the earlier measurements; for these reasons the difference in the salinity scales has been neglected in comparing results.

A comparison between the old and new results was made at 35‰ salinity, their common salinity. "Best" polynomial fits to both the new data and the earlier adjusted data at 35.009 and 35.00‰, respectively, were found by least squares procedures for fitting polynomials, in which the coefficients of the high-order terms in pressure and temperature are tested for their statistical significance. The fit to the earlier data at 35.00‰ was then adjusted to 35.009‰ using the formula previously fit to these data [5]. The differences between the fits and the standard errors of these differences are given in Table IV. The largest difference shown, at 5°C and 1000 bars, is equivalent to a salinity error of 0.006‰. In general, the differences are significant. They are most likely due to systematic errors in the temperatures of the older measurements; however, they do lie within the estimated accuracy of these results (better than the equivalent of 0.01‰ salinity).

FORMULAS FOR THE PRESSURE EFFECT ON THE ELECTRICAL CONDUCTIVITY OF SEAWATER

The entire set of results, both old and new, for the pressure effect on the electrical conductance of seawater have been analyzed and fitted by the method of least squares by Dauphinee [3] and by Lewis and Perkins [2] to rational functions of the form

$$\alpha = \frac{f_1(p, T, R)}{1 + f_2(T, \sqrt{R}, R)}$$

where α is the fractional increase in the electrical conductivity $C(S, T, p = 0)$ at constant salinity $S(^0/_{00})$ and temperature $T(^\circ\mathrm{C}$, IPTS-68) for an applied pressure p (decibars); $R = C(S, T, p)/C(35, 15, 0)$; and $f_1(p, T, R)$ and $f_2(T, \sqrt{R}, R)$ are polynomials. For the sake of completeness, their results are repeated here.

Oceanographic fit:

$$\alpha = \frac{A_1 p + A_2 p^2 + A_3 p^3}{1 + B_1 T + B_2 T^2 + B_3 R + B_4 R T}$$

where

$$A_1 = 2.070 \times 10^{-5}$$
$$A_2 = -6.370 \times 10^{-10}$$
$$A_3 = 3.989 \times 10^{-15}$$
$$B_1 = 3.426 \times 10^{-2}$$
$$B_2 = 4.464 \times 10^{-4}$$
$$B_3 = 4.215 \times 10^{-1}$$
$$B_4 = -3.107 \times 10^{-3}.$$

Standard deviation is 1.3 ppm in salinity.

General fit:

$$\alpha = \frac{A_1 p + A_2 p^2 + p^3(A_3 + A_4 T + A_5 T^2 + A_6 R + A_7 R P + A_8 R^2)}{1 + B_1 T + B_2 T^2 + B_3 T^3 + B_4 \sqrt{R} + B_5 R + B_6 T\sqrt{R} + B_7 T^2 \sqrt{R}}$$

where

$$A_1 = 1.76500 \times 10^{-5}$$
$$A_2 = -5.4149 \times 10^{-10}$$
$$A_3 = 2.191 \times 10^{-15}$$
$$A_4 = 2.508 \times 10^{-17}$$
$$A_5 = -1.729 \times 10^{-18}$$
$$A_6 = 3.818 \times 10^{-15}$$
$$A_7 = 7.517 \times 10^{-17}$$
$$A_8 = -2.846 \times 10^{-15}$$
$$B_1 = 3.6062 \times 10^{-2}$$
$$B_2 = 3.774 \times 10^{-4}$$
$$B_3 = 1.754 \times 10^{-6}$$
$$B_4 = -4.0658 \times 10^{-1}$$
$$B_5 = 6.3482 \times 10^{-1}$$
$$B_6 = -1.0576 \times 10^{-2}$$
$$B_7 = -3.465 \times 10^{-5}.$$

Standard deviation is 1.3 ppm in salinity.

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The authors wish to thank N. L. Brown for advice on the principles of measuring the electrical conductivity of seawater using four-electrode conductivity cells. We wish to acknowledge the work of R. G. Perkin, E. L. Lewis, and T. M. Dauphinee in fitting equations to both the data on the temperature effect on the electrical conductivity of standard seawater and that on the pressure effect on the electrical conductivity of seawater. Thanks are also due N. P. Fofonoff for his encouragement and for his suggestions as to the scope of the work.

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CONDUCTIVITY RATIO MEASUREMENT OF DILUTED OR CONCENTRATED STANDARD SEAWATER AND KCl SOLUTION USED TO ESTABLISH THE NEW PRACTICAL SALINITY SCALE, 1978

by

Alain POISSON*

(Submitted to Unesco for publication on 9 March 1981)

* Laboratoire de Physique et Chimie Marines, Université Pierre et
Marie Curie, Tour 24, 4 Place Jussieu, 75230 Paris Cedex 05, France.

INTRODUCTION

The principle of the determination of conductivity used in our laboratory consists of measuring the resistance of the solution with a Wheatstone bridge using alternating current.

The technical procedure consists of measuring the resistance R and the temperature t of a definite volume of seawater. The resistance is measured with a Jones type bridge (Leeds and Northrup, type 4666), the temperature with an A.C. bridge (A.S.L., type H7) and a platinum resistance (Tinsley, type 5187 SA), and the volume of seawater is defined by means of a Jones type cell (Beckman, type 6J). The dimensions of this cell (or the defined volume of seawater) can be determined by using KCl standard solutions (Jones and Bradshaw, 1933), whose specific conductivity is known with a great accuracy; these solutions are used as electrical conductivity standard solutions by physical-chemists.

The measured resistance R is :

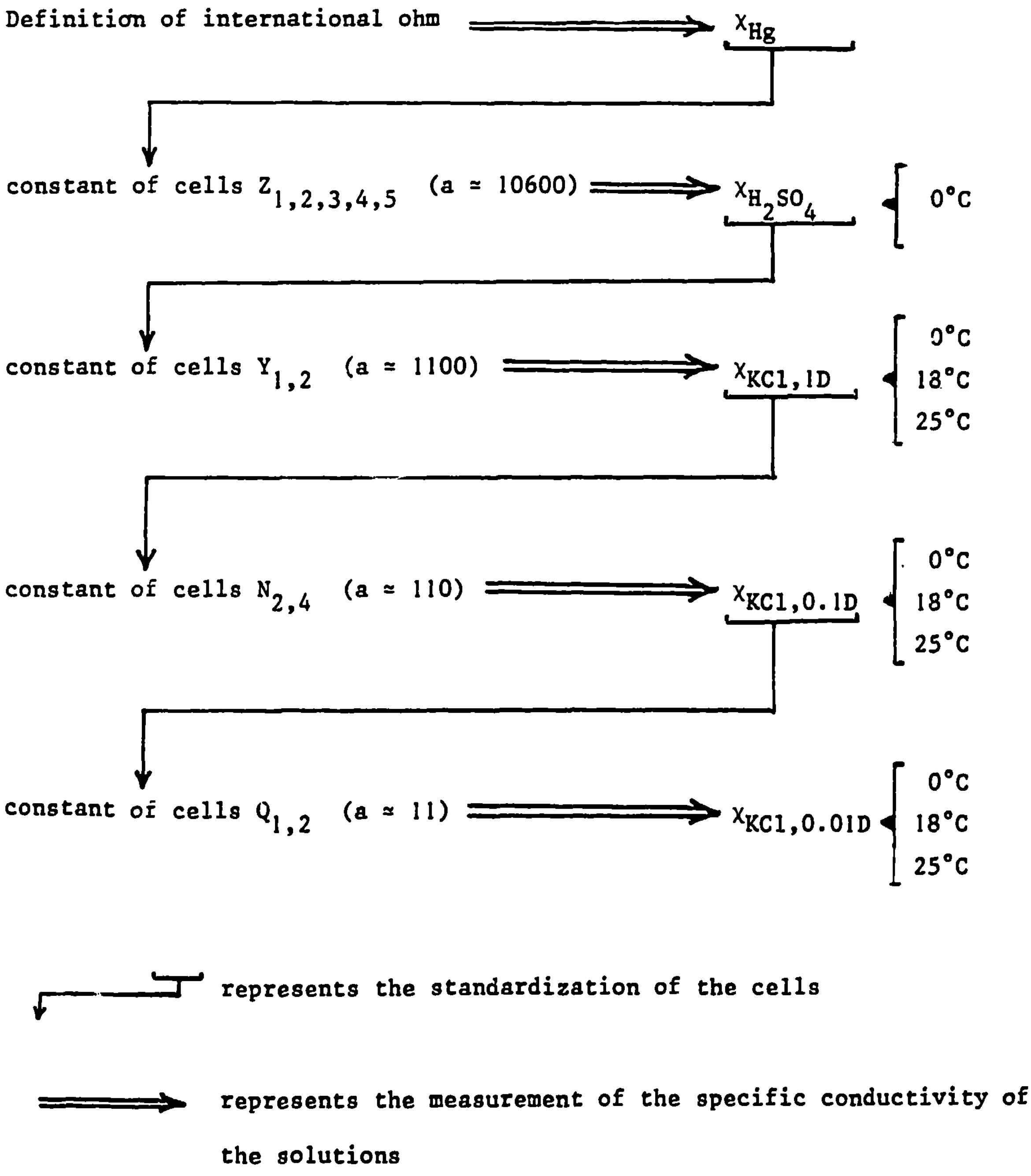
$$R = \frac{1}{\chi} \frac{\ell}{s} = \frac{a}{\chi} \qquad (1)$$

where $\chi(\Omega^{-1}\ cm^{-1})$ is the specific conductivity of seawater; $\ell(cm)$ is the length and $s(cm^2)$ the cross sectional of the volume of seawater; the ratio $\ell/s\ (cm^{-1})$, specific of the cell, is the constant "a" of the cell which defines its dimensions.

1. ELECTRICAL CONDUCTIVITY OF STANDARD SOLUTIONS

1.1. Summary of the work of Jones and Bradshaw (1933)

The international ohm being defined in terms of the specific resistivity of mercury, Jones and Bradshaw (1933) measured the conductivity of three KCl solutions by using this metal to standardize the fixed geometry cell they used. But as the conductivity of mercury and KCl solutions are very different, they used sulfuric acid as a liquid with intermediate conductivity. Their method is schematically represented hereunder :



The concentration of KCl solutions, in grams (in vacuum) of KCl per kilogram (in vacuum) of solution have been called "demal" (D) by these authors.

The solutions of KCl were prepared very carefully by a procedure described in detail in their paper. The specific conductivity of the water used to make these solutions was subtracted from the total conductivity of the 0.1D and 0.01D solutions.

We have used their results (Table 1) and their procedure as references to standardize our cells. It should be noted that the constant of the cells has been used only for the determination of the specific conductivity of seawater, and for the conductivity corrections during the measurements, but its value is not necessary to obtain the conductivity ratio.

Table 1 : Specific conductivity of KCl solutions by Jones and Bradshaw

demality	weight of KCl(g) per kg of solution(in vacuum)	χ_{KCl} (Ω^{-1} cm^{-1})		
		0°C	18°C	25°C
1D	71.1352	0.06517_6	0.09783_8	0.11134_2
0.1D	7.41913	0.007137_9	0.011166_7	0.012856_0
0.01D	0.745263	0.0007736_4	0.0012205_2	0.001408_7

1.2. Preparation of the KCl standard solutions, Jones and Bradshaw type

All the solutions were prepared with KCl suprapur (Merck) and doubly distilled water, using a method very similar to that of Jones and Bradshaw.

1.2.1. Purification of KCl and water

The water is distilled on tinned copper, then distilled again on quartz by accelerated evaporation, without ebullition. It is then kept for a few days in a flask so that the ambient air can dissolve in it until equilibrium is reached.

The potassium chloride is recrystallized three times, dried, then melted in a platinum crucible (Figure 1). This has enabled us to verify that the KCl is of sufficient parity for the preparation of solutions of the required accuracy. Thus KCl was then used without further purification to prepare the solutions which have been used to standardize standard sea-water (determination of the point 35 of the new Practical Salinity Scale, 1978).

1.2.2. Weighings of KCl and water

Weighings were carried out with Mettler balances type M5 and B5C1000. As the concentrations of the solutions are expressed in weight in vacuum, we have directly calculated this weight in vacuum (M) which is determined in our laboratory for the Mettler balances by

$$M = \frac{m(1 + 11.8\ 10^{-6})(1 - \frac{a}{7.76})}{1 - \frac{a}{\rho}} \qquad (2)$$

where ρ is the absolute density ($g.cm^{-3}$) of the body to be weighed and m its weight in air whose absolute density a is given by

$$a = \mathcal{M}(p + 0.21 - 0.3779\ f.h + c) \qquad (3)$$

where $\mathcal{M}$ = mass (g) of one cubic decimeter of dry air with 0.0004% of CO_2, at a pressure of 1mm Hg (Handbook of Chemistry and Physics, Chemical Rubber Co.),

p = atmospheric pressure (mm Hg),

f = pressure of the water vapor (mm Hg) in air at the temperature of the measurement (tables in literature give directly 0.3779f),

c = standard correction for the barometer measured at the Bureau International des Poids et Mesures (BIPM), Sèvres, and

h = relative humidity (%) of air.

1.2.3. Preparation of the standard KCl solution and calculation of its concentration

The different steps of the preparation of the KCl solution consist of the following :

- weighing the platinum crucible in air $a_1(t_1, h_1, p_1)$ and calculating its weight in vacuum (M_{pt}) by using the above-mentioned relations 2 and 3;

- melting KCl in the platinum crucible which is then put directly in a desiccator;
- weighing KCl in the platinum crucible in air $a_2(t_2, h_2, p_2) \Longrightarrow m_2^{total}$;
- calculating the apparent weight of the platinum crucible in air $a_2 \Longrightarrow m_2^{pt}$;
- calculating the apparent weight of KCl in air $a_2(m_2^{KCl})$ by

$$m_2^{KCl} = m_2^{total} - m_2^{pt} \ ;$$

- calculating the weight of KCl in vacuum (M_{KCl}) with the above-mentioned relations 2 and 3;
- calculating the weight of the water in vacuum (M_w) to be added to M_{KCl} grams of KCl in vacuum to obtain a KCl solution with a concentration D (in grams of KCl in vacuum per kilogram of solution in vacuum) :

$$M_w \text{ to be added} = M_{KCl} \left(\frac{1000}{D} - 1 \right) \ ;$$

- calculating, with the relation 2 and 3, the apparent weight of water to be added in air $a_3(t_3, h_3, p_3)$ at the moment of weighing the solution $\Longrightarrow m_3^w$;
- introducing the crucible containing the KCl together with a P.T.F.E. covered stirring magnet in a 1 litre flask which is then weighed in air $a_3 \Longrightarrow m_3^{flask}$;
- adding a quantity of doubly distilled water as near as possible to m_3^w ;
- weighing the flask containing the crucible, KCl, stirring magnet and water in air $a_3 \Longrightarrow m_3^{total}$;
- calculating the apparent weight in air a_3 of water by

$$m_3^w = m_3^{total} - m_3^{flask} \ ;$$

- calculating the weight in vacuum of water (M_w) by the relations 2 and 3;
- calculating the exact concentration of the KCl solution by

$$D = \frac{M_{KCl} \times 1000}{M_{KCl} + M_w} \ . \quad \text{(g KCl/kg solution)} \qquad (4)$$

This concentration is not exactly the same as the KCl solution of Jones and Bradshaw (Table 1) that was needed to determine the constant of the cell, so four solutions were prepared, and their resistances were

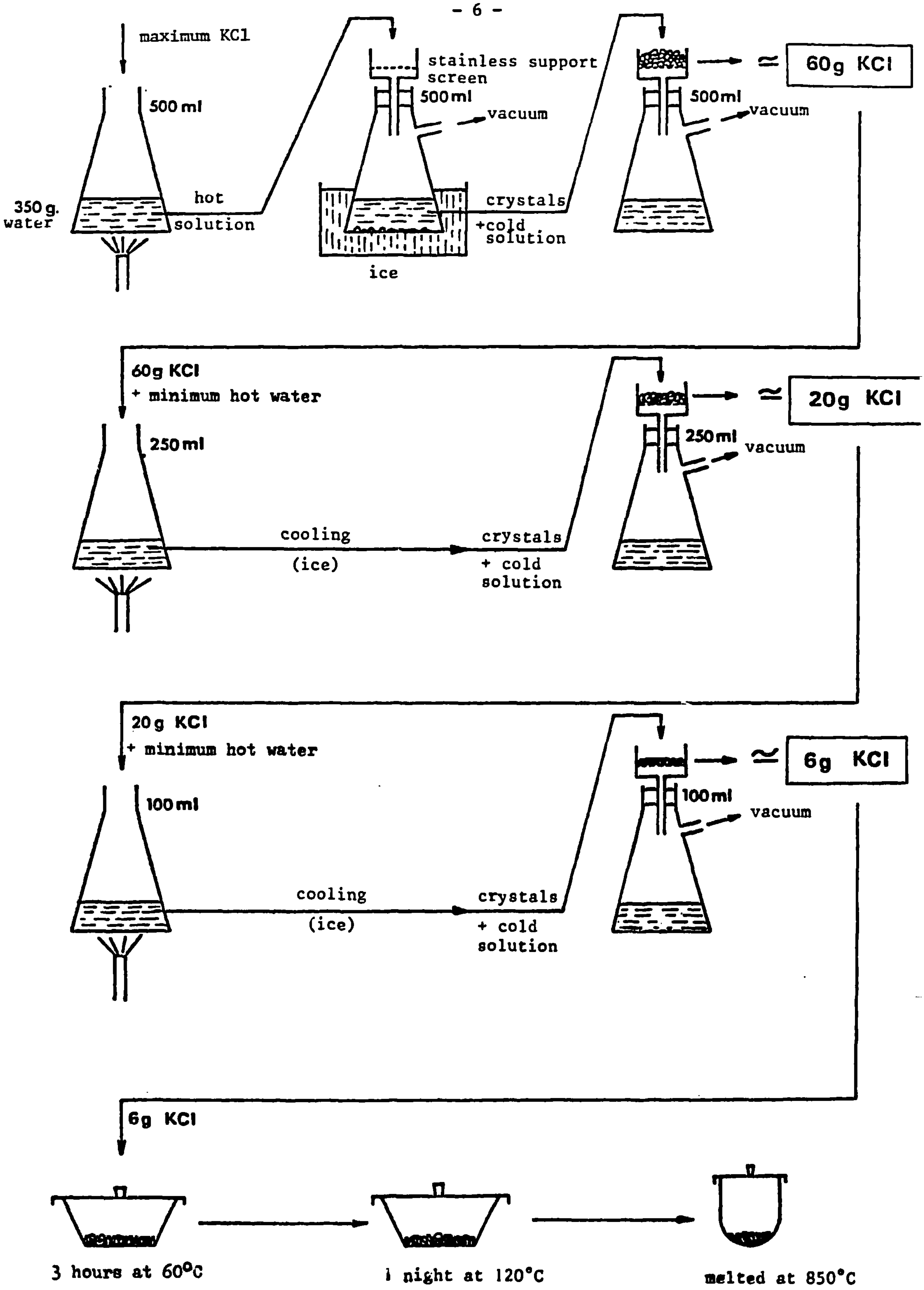


FIGURE 1 : Procedure for purification of KCl

measured. The resistance of the cell which corresponds to the exact concentration of Table 1, obtained by a linear regression, permits the calculation of the constant of the cell.

It is important to note that the constant of the cell is needed only for the determination of the specific conductivity of seawater and for the small corrections to be applied in the determination of the conductivity ratios (conductivity of the solution and of standard seawater must be determined at exactly the same temperature).

2. KCl SOLUTIONS USED TO DETERMINE THE CONCENTRATION OF THE SOLUTION HAVING, AT 15°C, THE SAME CONDUCTIVITY AS STANDARD SEAWATER ($S^o/oo = 35$)

The purification of KCl which is described in the previous paragraph has shown that the purity of KCl "suprapur" (Merck) was sufficient for the purpose of this work, and so it has been used directly to prepare the different KCl solutions. The KCl salt was dried either at 150°C for 24h under vacuum, or by melting. The latter method can be summed up as follows : the platinum crucible is weighed with a M5 Mettler balance, in air $a_1(t_1,h_1,p_1)$; its weight in vacuum M_{pt} is calculated with relations 2 and 3. A suitable amount of KCl is introduced into the crucible, then melted. The crucible is put immediately in a desiccator until its thermal equilibrium with room air is reached. Its weight m_2^{total} is measured with the M5 Mettler balance in air $a_2(t_2,h_2,p_2)$. The crucible containing the KCl is introduced in a 1 litre flask which is weighed (m_2^{flask}) with a B5C1000 Mettler balance. Distilled water is then introduced in the flask which is weighed (m_2^{w}) in air a_2.

M_{pt}, t_2, h_2, p_2, and relations 2 and 3 are then used to calculate the weight m_2^{pt} of the crucible in air a_2. With m_2^{pt}, m_2^{total} and relations 2 and 3, the weight M_{KCl} of KCl in vacuum is calculated directly. From m_2^{flask}, m_2^{w} and relations 2 and 3, the weight M_w of water in vacuum is calculated. The concentration C of the KCl solution can then be calculated from :

$$C = M_{KCl} \frac{1000}{M_{KCl} + M_w} \quad \text{g KCl/kg solution} \qquad (5)$$

As the flask is not entirely filled with the solution, a small amount of water (m_{vap}) evaporates in the air enclosed in the flask. The volume of this air is very close to the difference ' ..een the total volume V of the flask and the weight M_w of water introduced into the flask. The weight of evaporated water m_{vap} can then be calculated from

$$m_{vap} = \frac{18.001\ (V - M_w)\ p_w^{t_2}}{22415\ (1 + \frac{t}{273})\ 760} \qquad (6)$$

where $p_w^{t_2}$ is the partial pressure of saturated water vapor (mm Hg) at the temperature t_2. The exact calculation of the concentration of the KCl solution is then made with relation 5 where M_w is replaced by $M_w - m_{vap}$.

3. DILUTION AND CONCENTRATION OF STANDARD SEAWATER

3.1. Dilution

The dilutions have been made in screwed stopper flasks whose volume V_f is about 400 cm^3. The dilution is represented schematically in Figure 2 : doubly distilled water is first introduced (m_w) into the flask, the inside walls of which are moistened with this water so as to obtain air saturated with water vapor in the flask. A weight m_{sw} of seawater with salinity S_0 is then introduced into the flask, and the same volume of water-saturated air is then pushed out of the flask. The salinity of the diluted seawater is then calculated by using the true weight of liquid water which is in the flask and the weight of seawater introduced in the flask. Because the density of water and seawater are near unity, and all the weighings are made in a short period (and at the same temperature, pressure and relative humidity of air), it is not necessary to make air buoyancy corrections to the weights. m_0, m_1 and m_2 are directly measured with a B5C1000 Mettler balance. To calculate the salinity of diluted seawater, it is necessary to determine the weight of water vapor driven out of the flask while introducing seawater. As shown in Figure 2, we can write :

$$m_1 = m_0 + m_w + m_{vap_1} \qquad (7)$$

where m_w is the weight of liquid water in equilibrium with the weight m_{vap_1} of water vapor in the flask before the introduction of seawater. In the same way

$$m_2 = m_0 + m_w + m_{sw} + m_{vap_2} \qquad (8)$$

where m_{sw} is the weight of seawater introduced, and m_{vap_2} is the weight of water vapor in the flask in equilibrium with diluted seawater whose salinity S is

$$S = S_0 \frac{m_{sw}}{m_w + m_{sw}} \quad . \tag{9}$$

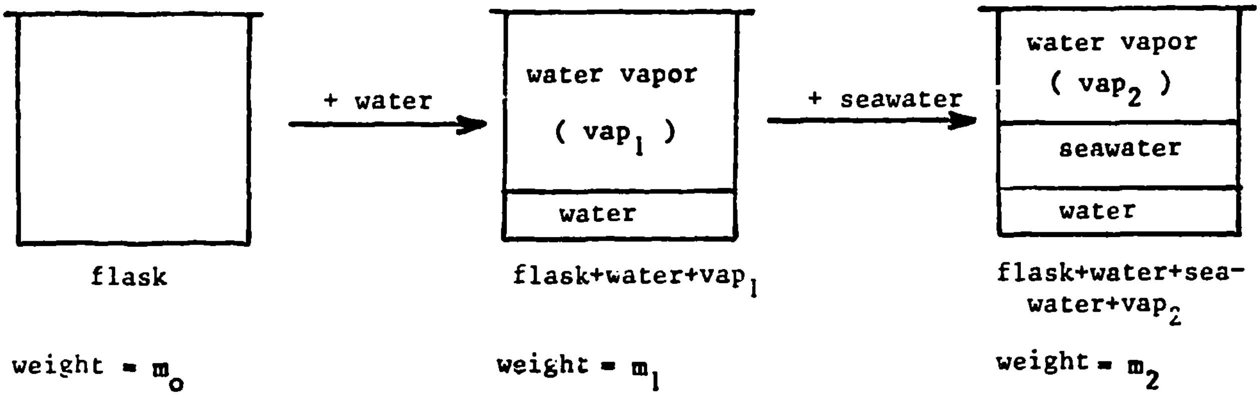


FIGURE 2 : DILUTION OF STANDARD SEAWATER

From equations 7, 8 and 9, we obtain

$$S = S_0 \frac{m_2 - m_1 + (m_{vap_1} - m_{vap_2})}{m_2 - m_0 - m_{vap_2}} \quad . \tag{10}$$

For this calculation, the volume of one mole of gas at 0°C is 22415 cm^3, its expansion coefficient $\alpha = 1/273 = 36.6\ 10^{-4}\ {}^{o}C^{-1}$ under a pressure of one atmosphere and the mass of the water molecule is 18.001g. The weight of the water vapor m_{vap_1} can be put in the form

$$m_{vap_1} = \frac{18.001\ (V_f - \frac{m_w}{\rho_w^t})\ p_w^t}{22415\ (1 + \frac{t}{273})\ p_{atm}^t} \quad , \tag{11}$$

where V_f is the volume of the flask, t is the temperature of room air during the weighings, p_w^t is the partial pressure of saturated water vapor at t°C, and p_{atm}^t is the atmospheric pressure at the same temperature.

In the following calculations, the absolute density of water and of seawater are equal to unity, and the atmospheric pressure is 760mm Hg; so,

$$m_{vap_1} = \frac{18.001\ (V_f - m_w)\ p_w^{\ t}}{22415\ (1 + \frac{t}{273})\ 760} \quad . \qquad (12)$$

In the same way, we would obtain

$$m_{vap_2} = \frac{18.001\ (V_f - m_w - m_{sw})\ p_w^{\ t}}{22415\ (1 + \frac{t}{273})\ 760} \qquad (13)$$

If we combine equations 12 and 13 with equation 10, and accept that $m_w \simeq m_2 - m_1$ and $m_{sw} + m_w \simeq m_2 - m_0$, we obtain

$$S = S_0 \frac{(m_2 - m_1)\ \{\ 62400\ (273 + t) + 18.001\ p_w^{\ t}\ \}}{(m_2 - m_0)\ 62400\ (273 + t) - 18.001\ (V_f - m_2 + m_0)\ p_w^{\ t}} \quad . \qquad (14)$$

It is this relation which has been used to calculate the salinity S of the diluted seawater. $p_w^{\ t}$ has been taken from Table D-92 "Vapor pressure of water below 100°C" in the Handbook of Chemistry, 45th Edition.

3.2. Concentration

Seawaters with salinity above 35 have been obtained by the following method : standard seawater is first concentrated by evaporation with the apparatus shown in Figure 3, to a salinity up to 42. During the entire evaporation process, the seawater is in contact with only the small amount of air enclosed in the apparatus, which avoids a CO_2 supersaturation. Several batches of seawater, with salinity ranging from 34.8 to 42 are then prepared by diluting with doubly distilled water the concentrated seawater previously obtained by evaporation; the salinity of the latter is estimated with a Guildline Autosal salinometer. Salinities of diluted seawater are determined with the weight of distilled water and the seawater used to make them and with relation 14. The resistances R of the run of diluted seawaters are measured by the method described in the following paragraphs, and fitted to a polynomial

$$S = A_0 + A_1R^{1/2} + A_2R + A_3R^{3/2} \ .$$

This plot is then readjusted by making S = 35 correspond to the resistance of standard seawater, based on batch P75.

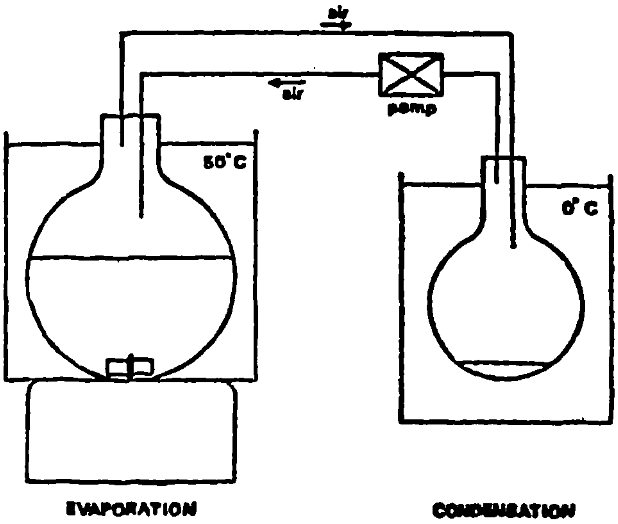


FIGURE 3 : SCHEMATIC DIAGRAM OF APPARATUS USED TO CONCENTRATE STANDARD SEAWATER

4. RINSING AND FILLING OF THE CONDUCTIVITY CELLS

The KCl solution (or the seawater) is placed in a humid box (relative humidity greater than 96%). The solution is transferred to the conductivity cell via a siphon. The cell is rinsed 4 or 5 times, then filled carefully so as to prevent the formation of micro air bubbles.

The resistance of this solution is measured first by the method described later, then the cell is refilled and the resistance is measured a second time. The two resistances are always within the experimental error.

5. APPARATUS

5.1. Resistance measurement

5.1.1. Jones type bridge : its principle

Electrical conductivity is the capability of a solution to transmit an electric current. Whereas in metals the electric current is carried by free electrons, in electrolyte solutions it is carried only by the ions. The determination of the electrolytic conductivity of a solution consists of measuring the resistance of a volume of the solution of known geometry. A Wheatstone bridge is used with A.C. current so as to eliminate the polarisation on the electrodes, which is a variation of the ionic composition of the solution due to the electrolytic reactions which can occur near the electrodes.

The bridge (Leeds and Northrup, type 4666) we used (Figure 4), set up by Jones (1933), is built in such a manner that the electrical conductivity of solutions can be measured with a high accuracy. The current strength, chosen to produce no measurable heating in the cell is given by an oscillator (Hewlett Packard, type 201 C).

Let E_1 be the alternating potential difference between A and B' (Figure 4) and I_1 the alternating current strength between A and B'. E_1 and I_1 are functions of time and can have a difference of phase; they are linked by the Ohm's law in alternating current :

$$E_1 = I_1 \, Z_1 = I_1 \, (R_1 + jX_1) \tag{15}$$

Z_1 is the impedance of the arm AB'

R_1 is the equivalent series resistance of the arm AB'

X_1 is the equivalent series reactance of the arm AB' which has the form :

$$X_1 = L_1\omega - \frac{1}{C_1\omega} \quad , \tag{16}$$

where L_1 is the inductance and C_1 the capacitance of the arm AB'; $\omega = 2\pi f$, where f is the number of cycles per second. Identical equations can be obtained for the three other arms of the bridge.

When the bridge is balanced, no current crosses the null detector (General Radio, type 1232 A); that is to say the potential in B is equal to the potential in B' at all times (the same numerical value and the same phase). This was achieved by using a Wagner earthing device, which ensures that the points B and B' of the bridge, the null detector

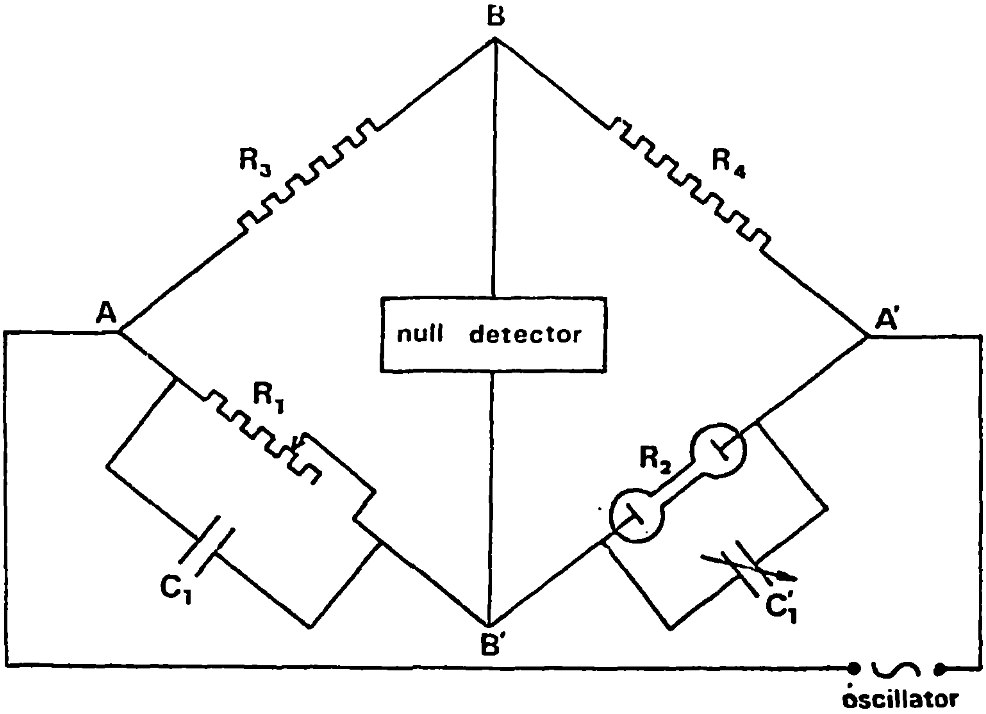


FIGURE 4 : SIMPLIFIED DIAGRAM OF JONES TYPE BRIDGE

and the operator are at the earth potential. Near balance, any current leakage which could occur between the earth, the operator and the arms of the bridge is eliminated. Then,

$$E_1 = E_3$$

$$E_2 = E_4$$

and

$$I_1 = I_3$$

$$I_2 = I_4$$

and

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4} \quad . \tag{17}$$

Now R_3 and R_4 are equal and as pure as possible; then,

$$Z_1 = Z_2 \quad . \tag{18}$$

But, although the reactance of the cell is very small, it is not negligible. That is why an adjustable reactance C_1 is introduced in parallel with the resistance box R_1 of the bridge (C_1 and C_1' are designed so that their effects are additive; so, we consider that C_1 is the sum of $C_1 + C_1'$ in the following development).

Conductivity cells

Conductivity measurements were carried out in Jones type cells (Beckman, type 6J). The most currently accepted electric diagram for this type of cell is shown in Figure 5.

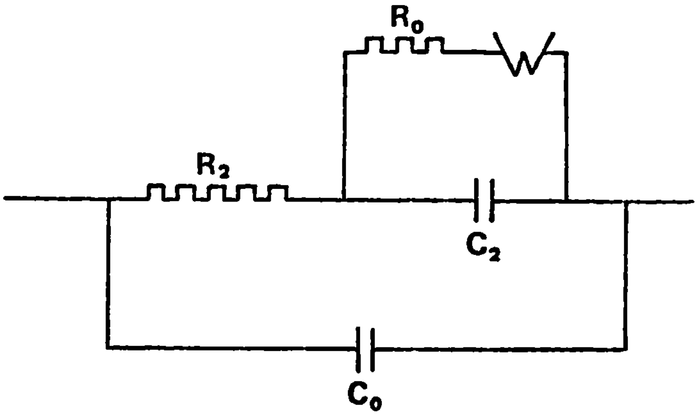


FIGURE 5 : EQUIVALENT ELECTRICAL DIAGRAM OF A CONDUCTIVITY CELL FILLED WITH AN ELECTROLYTIC SOLUTION

R_2 is the ohmic resistance of the solution which is between the electrodes; it is this value that we want to determine.

C_2 is the capacitance of the double layer which forms on the electrodes (non-faradic).

C_0 is the capacitance due to the solution which is between the two double layers.

W is the Warburg impedance (faradic type) due to the electrical reactions which occur on the electrodes.

R_0 is the resistance of the layer where the electrochemical reactions take place.

As we have seen in the previous paragraph, the impedances Z_1 and Z_2 are equal at balance. Now, for aqueous solutions in a cell with bright platinum electrodes,

$$R_2 >> R_0$$

and $$W << R_2 ;$$

Then, $$R_1 = R_2 + \frac{1}{1 + \omega^2 C_2^2 R_0^2} \qquad (19)$$

The measurement of R_1 at three different frequencies permits us to solve this equation with three unknown quantities. In practice, the linear extrapolation at infinite frequency of R_1 versus 1/f gives the same value. It is this practical method that we have used : the resistance is measured at 4 frequencies (2000 Hz, 2500 Hz, 3000 Hz and 4000 Hz) selected so as to obtain a perfect linear curve, whatever the resistance of the solution (Figure 6). By subtracting the resistance of the wires which link the electrodes and the bridge from the value of the extrapolated resistance ($f \rightarrow \infty$), we obtain the value of the ohmic resistance R_2 of seawater. The cells used have constants of 1, 30 and 120 cm^{-1}.

Standard resistances

The Jones bridge has been standardized with standard resistances (Leeds and Northrup, type N.B.S.) of 10, 100, 1000 and 10000 Ω. The value of these resistances, standardized at the Bureau International des Poids et Mesures (BIPM), Sèvres, is known with an accuracy greater than 0.0001%.

5.2. Temperature measurement and record

Thermostat

A 300 litres bath has been specially built for these measurements in our laboratory. The temperature can be stabilized at $\pm 1 \times 10^{-3}$ °C from -2^oC to 35^oC. The schematic diagram of this bath is shown on Figure 7. It is composed of 3 main parts :

- a cooler (Secasi, type 24 CY 45) with a maximum power of 1000 watt at 0^oC. A pump pushes the alcohol of this bath through a coiled tube which covers the walls of the cold bath.

- a cold bath which has a volume of about 75 litres. A contact thermometer monitors via a relay (Prolabo, type 03 905 12) a resistance

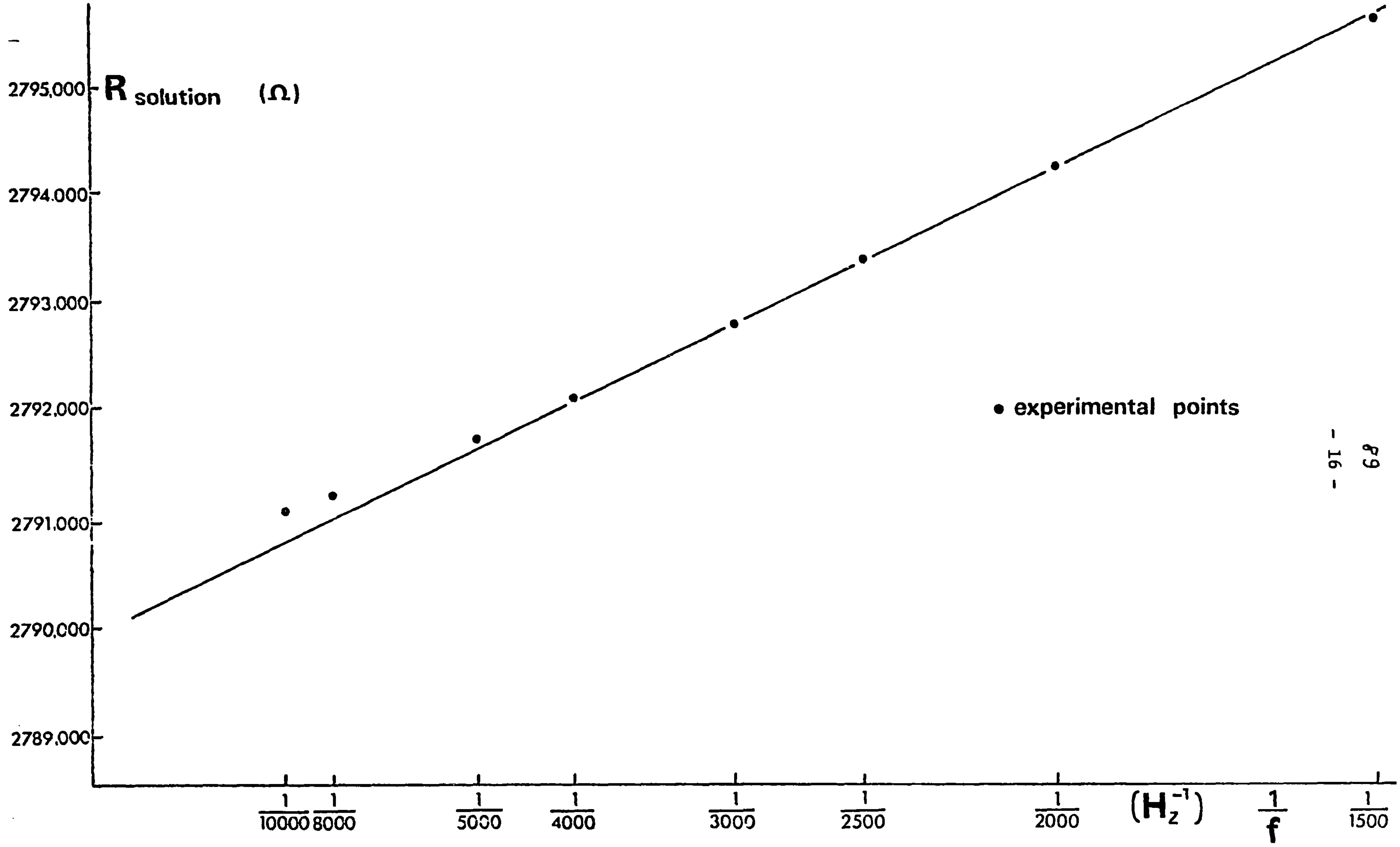


FIGURE 6 - STANDARD SEAWATER RESISTANCE VERSUS THE INVERSE OF THE CURRENT FREQUENCY

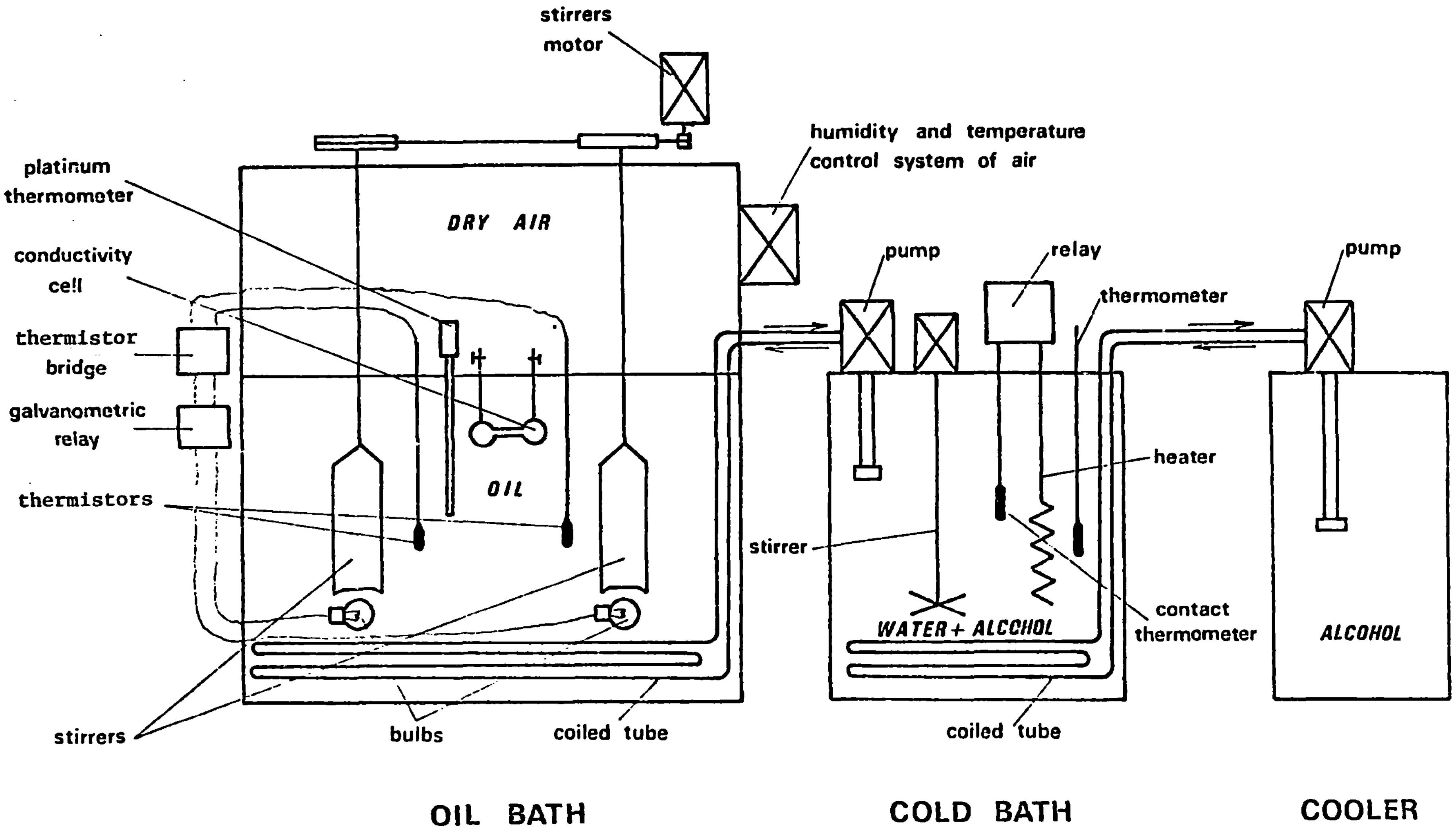


FIGURE 7 - THERMOSTATTED BATH USED FOR THE CONDUCTIVITY MEASUREMENTS

which stabilizes the temperature of the mixture "water + alcohol" to about ± 2×10^{-2} °C. The temperature of this bath is slightly lower than that of the oil bath. A pump pushes the liquid of this bath through a coiled tube which covers the walls of the oil bath.

- an oil bath containing about 300 litres of dry mineral oil (Solgil 156H) which is stirred very vigorously by two stirrers specially made for this purpose. The constant amount of frigories arriving in the oil bath (from the cold bath) is compensated for with heating provided by two electric bulbs of 100 W which are monitored by a galvanometer-relay (Sefram, type RGC). This relay is the null detector in a Wheatstone bridge whose 2 opposite arms are composed of a thermistor with a high thermal coefficient. The two other arms consist of a series of 100, 1000 and 10000 Ω resistances. The current, produced by a 6V dry cell adjusted with a resistance, imposes the intensity of the imbalance of the bridge which can be read on the galvanometer-relay. The surface of the oil in the bath is covered with weighted plastic balls to insulate the oil and to prevent the penetration of moisture in oil at low temperature. The bath is topped with an enclosure inside which the air is dried and thermostatted at a temperature slightly greater than the oil; this prevents the formation of condensation inside the emergent part of the cell, to prevent any evaporation of seawater during measurements.

Thermometric bridge and platinum thermometer

The temperature of the oil bath is measured with a high precision automatic inductive ratio arm bridge (ASL, type H7) by a platinum thermometer (Tinsley, type 5649) relative to a 10 Ω standard resistance R_{sdt} (Leeds and Northrup, type NBS-4025 B). This bridge measures the ratio $R_{sdt}/(R_{sdt} + R_{th})$ where R_{th} is the resistance of the platinum thermometer. This resistance is converted into degrees C of the 1968 International Temperature Scale. The bridge is balanced by hand, and a signal proportional to the variation of temperature is recorded on a Sefram recorder (type PED x 100). The sensitivity of the measurement is ± 1×10^{-4} °C and its accuracy ± 1×10^{-3} °C. The thermometer has been standardized, and the bridge checked at the BIPM. Each measurement of temperature is corrected for the energy dissipated by heating; the temperature is the one of International Practical Temperature Scale of 1968.

6. TECHNICAL PROCEDURE

6.1. Schematic description of the Jones bridge

The Jones type bridge has been specially built for very accurate measurements of the electrical conductivity of solutions. Resistances up to 60011 Ω can be obtained with 5 decades of 0.1 Ω, 10 Ω, 100 Ω and 1000 Ω and 5 switch-selected 10000 Ω resistors. These resistors are either woven or bifilar so that the effective A.C. resistance at 1000 Hz is within ± 0.001% of the D.C. value. To eliminate errors due to capacitance to ground, the bridge is provided with a modified form of the well known Wagner earthing device. Two adjustable air capacitors C_1 and C_2 (Figure 8) are included to compensate for the conductivity cell capacitance in making the phase-angle balance of the bridge. The ratio arms of the bridge are adjusted to equality with the adjustable slidewire resistor R_1 of 1 Ω. An adjustable bifilar resistor R_2, with a scale calibrated from -0.050 to +0.150 Ω (± 0.001 Ω), extends the range of the bridge below 0.1 Ω and permits a very precise balance of the bridge.

6.2. Standardization of the resistors of the bridge

The different steps of the standardization described below have been executed in the indicated order. During all the steps described, the temperature of the room is thermostatted and the relative humidity of air at 25°C is always less than 40%.

6.2.1. Cleaning of connection binding posts of the bridge

The smaller the resistance to be measured is, the more important it is to have very good contacts. For this reason, before each run of measurements, the binding posts of the bridge and of connection leads are ground with a fine grained sandpaper.

The binding posts of standard resistances used for the calibration of the bridge, those of the bridge S_1, S_2, X_1, X_2 and the ends of the two copper links used for shorting S_1S_2 and X_1X_2 are first carefully cleaned as recommended by the manufacturer : after having ground them with a fine grained sandpaper, they are moistened with water and covered with a sodium-mercury amalgam. They are then washed with distilled water and dipped into clean chemically-pure mercury. The contacts are then excellent when mercury adheres perfectly to the metal.

6.2.2. Checking of the zero point of the resistor R_2 of the bridge

It is with this resistor that the final balance of the bridge is made. Thus its zero point must be known with a high accuracy. A dry cell (1.5 V), an Ammeter (Sefram, type GP 4) and two boxes of resistances A.O.I.P. are used to adjust the current strength at the input of the bridge (Figure 8). The binding posts S_1S_2 and X_1X_2 are short-circuited. The shift ΔR_2 of the zero point of resistor R_2 is obtained by adjusting slidewire R_2 until the galvanometer (Sefram, type PS4 BD) reaches a balance.

ΔR_2 is determined 4 times; the mean of these 4 values is $\Delta R_2{}^0$.

6.2.3. Checking of the equality point of the ratio arms of the bridge

This check is carried out by using the bridge as described on Figure 8, but the slidewire R_2 is set at $\Delta R_2{}^0$ and the two links are replaced by 1000 Ω standard resistors (Leeds and Northrup, type 4035-B); the current strength is adjusted at 5.10^{-3}A in the circuit out of the bridge. The bridge is balanced by adjusting slidewire R_1 until the galvanometer reaches a balance; we read R_1-d. The same measurement is made but the 1000 Ω standard resistors are interchanged at S_1S_2 and X_1X_2; we read R_1-g.

These two measurements R_1-d and R_1-g are made four times. The mean ($R_1{}^0$) of these eight measured values is the unity point of the ratio arm of the bridge. The correction to apply on the slidewire R_1 is then $100 - R_1{}^0 - \Delta R_1{}^0$.

6.2.4. Measurement of the resistance of the connection leads A-B used for the standardization of the resistors of the bridge

This measurement is made by using the bridge as described on Figure 8, but the 1000 Ω standard resistors are replaced by two 10 Ω standard resistors (Leeds and Northrup, type 4025 B). The leads A-B are set

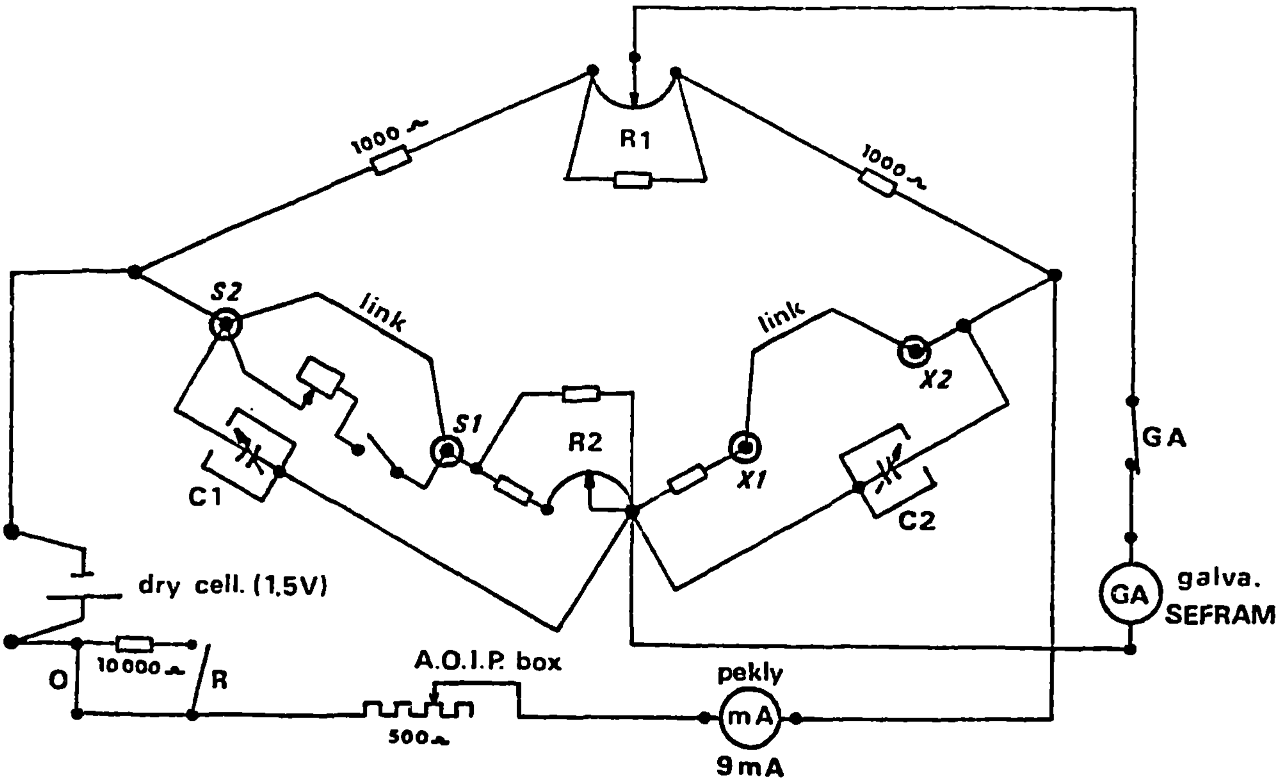


FIGURE 8 : EXPERIMENTAL DEVICE OF THE JONES BRIDGE FOR CHECKING OF THE ZERO POINT OF THE BRIDGE

in series with one of these 10 Ω resistors between X_1 and X_2; the connections between A-B wire and the resistor ends are made in containers filled with chemically-pure mercury. The current strength is 30 x 10^{-3}A in the circuit. A wire E-F, with a very small resistance (0.0035 Ω at 20°C) is placed between S_1 and X_1; its resistance is measured by the same method as the one described in this paragraph, but S_1 and X_1 are linked by a wire identical to E-F and the wire A-B is replaced by the wire E-F. Slidewire R_1 is adjusted until the galvanometer reaches a balance. We read R_1 on the bridge (R_1^{bridge}) and note the temperatures t_I and t_{II} of the standard resistors and t of room air.

The resistance of the wire A-B at temperature t is given by :

$$R^t_{A-B} = \left[\frac{R_1^{\text{bridge}} - \Delta R_1^0}{100}\right]\left[R_I^{20} \quad 1 + \alpha_I(t_I-20) + \beta_I(t_I-20)^2\right]$$

$$- R_{II}^{20}\left[1 + \alpha_{II}(t_{II}-20) + \beta_{II}(t_{II}-20)^2\right] \qquad (20)$$

where R_I^{20} and R_{II}^{20}, the resistances of standard resistors at 20°C have been measured at the BIPM and α_I, α_{II}, β_I and β_{II}, temperature coefficient constants of these resistors are given by the manufacturer. Between 18°C and 25°C, $R^t_{A-B} = 0.0022\ \Omega$ within $\pm\ 0.0001\ \Omega$.

6.2.5. Measurement of the resistors of the bridge

Each resistor of the bridge, R^t_{bridge} (10 Ω, 100 Ω, 1000 Ω and 10000 Ω resistors) is compared to a standard resistor (Leeds and Northrup) whose resistance is R^t_{Std} at t°C. This standard resistor is placed between S_1 and S_2 binding posts, and the bridge resistor to be measured is connected to binding posts X_1 - X_2 with the wire A-B (Figure 9). Current strength is adjusted at 30×10^{-3}A for the 10 Ω resistors, 11×10^{-3}A for the 100 Ω resistors, 6×10^{-3}A for the 1000 Ω resistors and 2.5×10^{-3}A for the 10000 Ω resistors. The current strength which goes through the standard resistor is then the same as the one used for its calibration at the BIPM. For each measurement R_1 is adjusted until the galvanometer reaches a balance and the temperature of the standard resistor (t_{Std}) and of the air inside the bridge

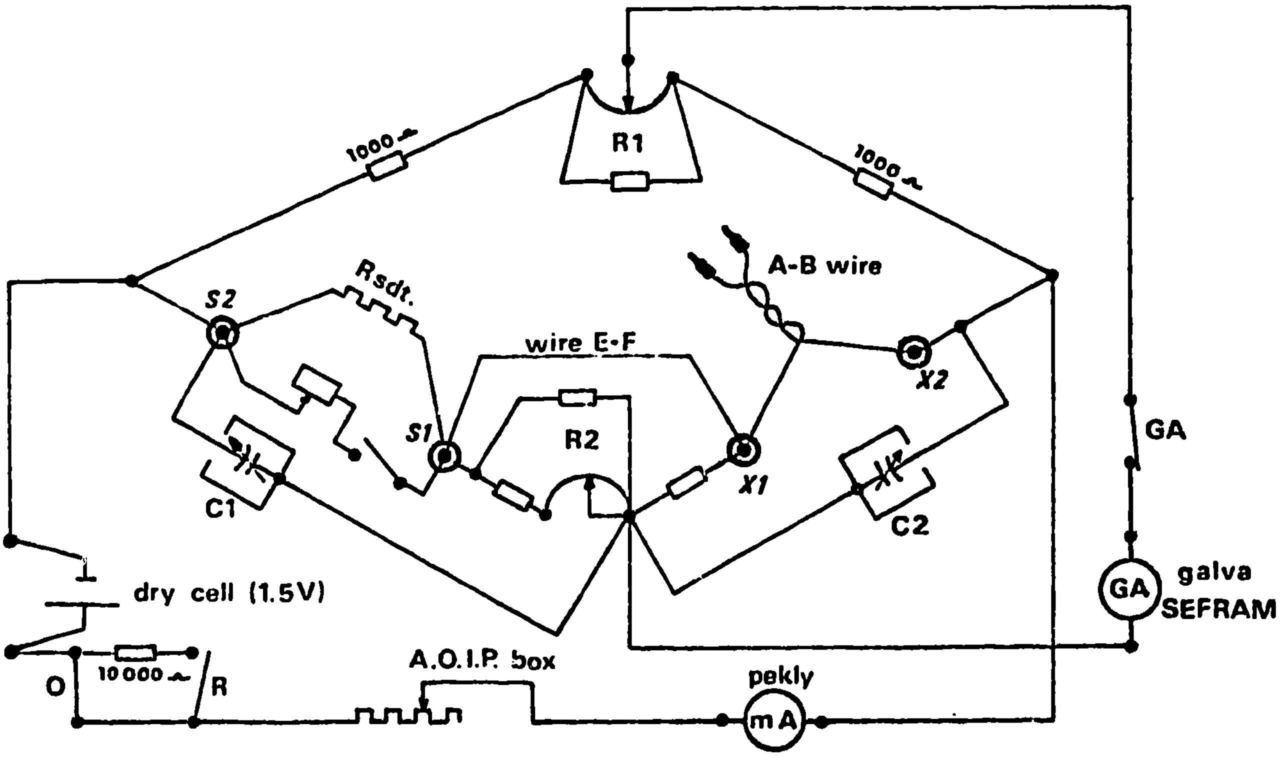


FIGURE 9 : EXPERIMENTAL DEVICE OF THE JONES BRIDGE FOR THE STANDARDIZATION OF ITS RESISTORS

case (t_{bridge}) are noted. The resistance R^t_{bridge} measured at temperature t is calculated by

$$R^t_{bridge} = R^{20}_{Std} \left[\frac{R_1^{bridge} - \Delta R_1^0}{100} \right] \left[1 + \alpha_I (t_{Std} - 20) + \beta_I (t_{Std} - 20)^2 \right] - R^t_{A-B} \quad , \qquad (21)$$

where R^{20}_{Std} has been measured at the BIPM and α_I, β_I are given by the manufacturer. Three runs of measurements have been made at temperatures of 20°C, 22.5°C and 25.5°C. These results have been fitted in polynomials of the form :

$$R^t_{bridge} = R^{20}_{bridge} \left[1 + \alpha_{20} (t_{bridge} - 20) + \beta_{20} (t_{bridge} - 20)^2 \right] \qquad (22)$$

which gives the resistance of each resistor of the bridge versus the temperature inside the bridge case.

6.3. Standardization of the conductivity cells

6.3.1. Measurement of the resistance of the solution between the cell electrodes

6.3.1.1. Measurement of the resistance of wires which connect the bridge to the cell electrodes

This measurement is made with D.C. current with the device used for the bridge resistors calibration (Figure 9). Between the binding posts X_1 and X_2, a resistor of the bridge is put in series (here between posts 2 and 3 of the 1000 Ω resistors) with the cell full of chemically-pure mercury, by using the connection wires and the lead A-B. The total resistance between X_1 and X_2 is the sum of the resistances of the bridge resistor (R^t_{bridge}), of the connection wires ($R^t_{conn.}$), of wire A-B (R^t_{A-B}) and of the mercury between the cell electrodes (R^t_{Hg}). R_1 is adjusted until a balance of the galvanometer is achieved; we measure the temperature of the bridge case (t) and of the oil bath containing the mercury-filled cell (t_b).

The resistance of connection wires ($R^t_{conn.}$) is calculated by :

$$R^t_{conn.} = \left[\frac{R_l^{bridge} - \Delta R_l^0}{100} \right] R^t_{Std} - R^t_{bridge} - R^t_{A-B} - R^{t_b}_{Hg} \qquad (23)$$

where the resistance of mercury is :

$$R^{t_b}_{Hg} = \rho_{t_b} \frac{\ell}{s} = \rho_{t_b} . a \quad ,$$

where "a" is the constant of the cell. $R^{t_b}_{Hg}$ is very small, so the constant "a" of the cell need not be known with a great accuracy. The resistivity of mercury ρ_{t_b} is given by

$$\rho_{t_b} = \rho_{20} \{ 1 + \alpha_{20} (t_b - 20) \}$$

with $\rho_{20} = 95.783 \; 10^{-6} \; \Omega \; cm^{-1}$

and $\alpha_{20} = 0.89 \; 10^{-3} \; {}^oC^{-1}$

6.3.1.2. Measurement of the resistance of KCl solution or seawater

This measurement is made using alternating current by using the device recommended by the manufacturer, but the cell electrodes are of bright platinum. For reasons shown before (§ 5.1), the resistance is measured at four frequencies (2000, 2500, 3000 and 4000 Hz), selected in order to obtain a straight line from these four points, whatever the seawater resistance is. That is to say that the measurements are made within the frequency area where only the migration current occurs. Each of these four points is obtained in the following manner : the temperature of the oil bath which varies within ± 1 x 10^{-3} °C with a mean period of about 2 min., is measured with the ASL thermometric bridge and recorded throughout the measurements (Figure 10). At times t_A, t_B, t_C and t_D, the resistances of the solution R_A, R_B, R_C and R_D are measured with the Jones bridge. The time constants of the conductivity cell and of the platinum thermometer regarding the variations of temperature are practically identical; then the mean resistance at a frequency of 2000 Hz, $R_{2000} = \frac{1}{4} (R_A + R_B + R_C + R_D)$ corresponds to the average temperature $t_m = \frac{1}{4} (t_A + t_B + t_C + t_D)$.

The pure resistance of the solution, $R_{sol}^{t_m}$, at the temperature t_m, is then calculated by using the value of R for the infinite frequency of the four measurements (R_{2000}, R_{2500}, R_{3000}, R_{4000}) from which the resistance of the connection wires $R_{conn.}^{t}$ is subtracted.

6.3.2. Determination of the resistance of KCl standard solution

The conductivity of the KCl solution, χ_{sol}, is the sum of the potassium chloride conductivity, χ_{KCl}, and that of water χ_w. The distilled water used to make the standard KCl solution was in equilibrium with air, which permits us to work on these solutions without any special precautions on the gas exchange between the solution and air. But in this case it is necessary to know the conductivity of the distilled water because it is not negligible relative to the conductivity of low concentration KCl solutions.

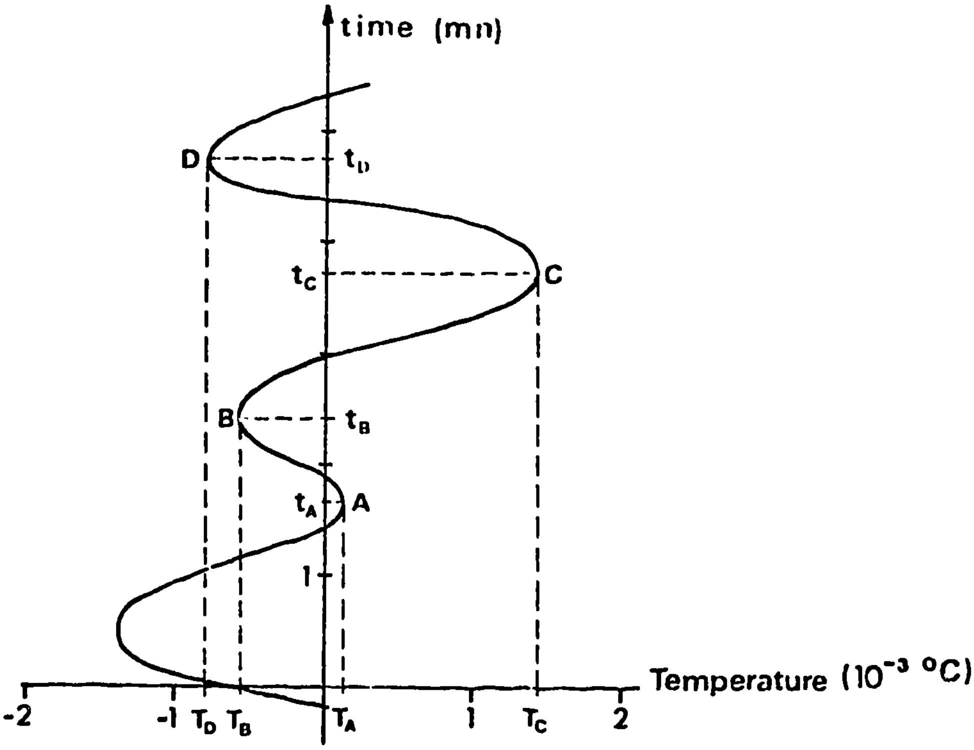


FIGURE 10 : VARIATION OF TEMPERATURE DURING A MEASUREMENT OF RESISTANCE

6.3.2.1. Measurement of water conductivity (method of Justice, personal communication)

The equivalent conductance of KCl in aqueous solution is :

$$\Lambda_{KCl} = \frac{1000\ \chi_{KCl}}{C} \quad , \tag{26}$$

where C is the concentration (eq.1^{-1}) of the solution and χ_{KCl} the conductivity of KCl in the solution.

We can write :

$$\chi_{KCl} = \chi_{sol} - \chi_w = \frac{\Lambda_{KCl}\ C}{1000} \tag{27}$$

Now, with the Jones bridge, we measure the resistance of the solution $R_{sol} = a/\chi_{KCl}$ and the resistance of water $R_w = a/\chi_w$ where "a" is the constant of the cell. Then

$$\frac{\Lambda_{KCl}\ C}{1000} = a\ \left(\frac{1}{R_{sol}} - \frac{1}{R_w} \right) \tag{28}$$

If we write

$$\frac{\Lambda_{KCl}\ C}{1000} = \frac{a'}{R_{sol}}$$

we obtain

$$a' = a\ (1 - \frac{R_{sol}}{R_w})$$

and

$$a' = a - R_{sol}\ \chi_w \tag{29}$$

a' is plotted versus R_{sol} to obtain "a" for $R_{sol} = 0$; the slope of the curve gives χ_w. We have used the Fuoss and Onsager relation put in the numerical form (Lind et al., 1959)

$$\Lambda_{KCl} = 149.93 - 94.65\ C^{1/2} + 58.74\ C\ \log C + 198.4\ C \tag{30}$$

which is verified for $C < 0.012$ N.

It is possible to convert the "demality" D (mole/1000g solution) into concentration C (eq/l) with the relation

$$C/D = 0.99707 - 0.0272\ D. \qquad (31)$$

Here, the molecular weight of KCl is 74.557g.

A solution of KCl (C = 0.01 N) with a known concentration (determined by weight) is diluted and its resistance R_{sol} is measured at each dilution. a' is deduced from these measurements and the above mentioned relations. The constant "a" of the cell and the specific conductance of pure water are then determined in only one run of measurements.

6.3.2.2. Determination of the specific conductivity of the standard

Instead of preparing one solution whose concentration is exactly the one given by Jones and Bradshaw, it is easier and more accurate to prepare four solutions close to this value. The resistance of these solutions is determined as described above (§ 6.3.1.) and the resistance $R^t_{Std\ sol}$ corresponding to the exact concentration is obtained by a linear regression.

6.3.3. Calculation of the constant of the cell

The specific conductivity of the KCl standard solution ($\chi_{Std\ sol}$) is :

$$\chi_{Std\ sol} = \chi_{KCl} + \chi_w = a/R^t_{Std\ sol} \qquad (32)$$

χ_{KCl} is given in Table 1, χ_w has been determined in section 6.3.2.1. and $R^t_{Std\ sol}$ in the preceding section.

The constant of the cell is then easily calculated and we can determine the specific conductance of seawater.

6.4. Determination of the specific conductance and conductivity ratio of seawater

As shown in the previous sections, if we know the constant "a" of the cell and the resistance of seawater R_{sw} at temperature t, it is possible to calculate directly the specific conductance χ_{sw} by $\chi_{sw} = a/R_{sw}$.

For standard seawater (S = 35), in the same way we have $\chi_{std} = a/R_{Std}$ at the same temperature.

The conductivity ratio of seawater R_t is

$$R_t = \frac{\chi_{sw}}{\chi_{Std}} = \frac{R_{Std}}{R_{sw}} \qquad (33)$$

Thus, the error made on the determination of the constant of the cell is eliminated when determining the conductivity ratios. It is only for the specific conductance and for some corrections that we need the constant of the cell.

7. CALCULATION OF THE COEFFICIENTS OF A POLYNOMIAL DESCRIBING THE MEAN SURFACE FITTED WITH N EXPERIMENTAL DATA*

To compare our results with those of previous works, we have fitted our data into polynomials which describe the measured quantities, for example salinity versus temperature and conductivity ratio. To calculate the coefficients of these polynomials, we have used the following method :

Let N triplets of values (x, y, z) correspond to N measurements. z is the measured physical quantity and is a function of x and y. We want to approximate the value z of the triplet with a function P such as

$$\frac{P}{U} + C = \sum_{i=0}^{k} \sum_{j=0}^{i} a_{(i-j,j)} x^{(i-j)} y^{j} \qquad (34)$$

where U and C are functions of x and y or any constants which constrain the surface described by P to go through curves given a priori. These curves can be absolute references, or proceed from the definition of variables used in the calculation. P/U + C is a polynomial of x and y, and its power is k.

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* This method has been developped in our laboratory by J. C. Brun Cottan.

N must satisfy the condition :

$$N \leqslant \frac{(k+1)(k+2)}{2} \tag{35}$$

There are $\frac{(k+1)(k+2)}{2}$ coefficients ($a_{\alpha,\beta}$) of P/U + C to be calculated such as the sum ζ of squared deviations between P and Z is reduced to a minimum. The deviations are considered in a parallel direction of z axis, and ζ has the form :

$$\zeta = \sum_{n=1}^{N} W_n \, (P - Z_n)^2 \tag{36}$$

where W_n is a weighing law on x and y. At the minimum of ζ, the derivatives $\partial\zeta/\partial a_{\alpha,\beta}$ are null; they can be written

$$\frac{\partial \zeta}{\partial a_{\alpha,\beta}} = 2 \sum_{n=1}^{N} W_n \, (P - Z_n) \, U_n x_n^{\alpha} \, y_n^{\beta} = 0 \quad . \tag{37}$$

Then,

$$\sum_{n=1}^{N} W_n U_n P \, x_n^{\alpha} \, y_n^{\beta} = \sum_{n=1}^{N} W_n \, U_n (Z_n - C_n) x^{\alpha} y^{\beta} \quad . \tag{38}$$

Then,

$$\sum_{n=1}^{N} W_n \, U_n^2 \sum_{i=0}^{k} \sum_{j=0}^{i} a_{(i-j,j)} x_n^{(i-j)} \, y_n^{j} \, x^{\alpha} \, y^{\beta} =$$

$$\sum_{n=1}^{N} W_n U_n (Z_n - C_n) \, x_n^{\alpha} y_n^{\beta} \tag{39}$$

This equation can be written under the form :

$$\sum_{i=0}^{k} \sum_{j=0}^{i} \sum_{n=1}^{N} W_n^2 \, U_n \, a_{(i-j,j)} \, x_n^{(i-j+\alpha)} \, y_n^{(j+\beta)} =$$

$$\sum_{n=1}^{N} W_n \, U_n (Z_n - C_n) \, x_n^{\alpha} \, y_n^{\beta}.. \tag{40}$$

The whole $\frac{(k+1)(k+2)}{2}$ equations are a system AX = B where we want to determine A = BX. The elements e of the square matrix X, whose dimension is k x k, to inverse, are :

$$e_{[(\alpha,\beta),(i-j,j)]} = \sum_{n=1}^{N} W_n \, U_n^2 \, x_n^{(i-j+\alpha)} \, y_n^{(j+\beta)} \tag{41}$$

and the elements b of the column matrix B, whose dimension is k, are :

$$b_{(j,\beta)} = \sum_{n=1}^{N} W_n \, U_n (Z_n - C_n) \, x_n^{\alpha} \, y_n^{\beta} \tag{42}$$

The absolute mean square deviation σ is

$$\sigma = \left[\frac{1}{N} \sum_{n=1}^{N} (P - Z_n)^2 \right]^{1/2} \tag{43}$$

and the relative mean square deviation σ_r is

$$\sigma_r = \left[\frac{1}{N} \sum_{n=1}^{N} \left(\frac{P - Z_n}{Z_n} \right)^2 \right]^{1/2} \tag{44}$$

σ_r is interesting when a weighing law of the type

$$W_n = \frac{1}{(x_n \, y_n)^p} \qquad \text{with } p > 0 \tag{45}$$

is introduced.

The appearance of high power terms in x and y can produce as a consequence a badly-conditioned matrix X. To avoid this possible disadvantage, the calculations have been made in double precision, i.e. 15 significant decimal digits (C.I.I. computer, type IRIS 80). The calculation of coefficients $a_{\alpha,\beta}$ is made a second time but the values Z_n are replaced by the values P determined in the first calculation. In this second calculation σ must theoretically be equal to zero. But, due to the limit of precision of the computer, σ is not exactly equal to zero in the second calculation. In our calculation, it has been always smaller than 10^{-10}, which is largely sufficient for the accuracy we needed.

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FITTING OF THE DATA

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The Practical Salinity Scale 1978: Fitting the Data

RONALD G. PERKIN AND EDWARD LYN LEWIS

Abstract—**Three equations have been fitted to new data relating the electrical conductivity of seawater to the Practical Salinity Scale 1978. These equations have been designed for the reduction of *in-situ* measurements of temperature, pressure, and conductivity from anywhere in the world oceans. The standard deviation of the fit is roughly equivalent to ±0.0015‰ in salinity depending on the pressure at which the data is taken and, as such is commensurate with the best accuracy attainable with modern instruments.**

INTRODUCTION

THE PRACTICAL Salinity Scale 1978 is based on an equation relating salinity to the ratio of the electrical conductivity of seawater at 15°C to that of a standard potassium chloride solution (KCl). In order to obtain a basis for the relationship between oceangraphic variables on this new scale, ampoules of standard seawater prepared at the Institute of Ocean Sciences, Wormley, England, were distributed to a number of investigators. These workers measured the conductivity ratios of by weight evaporated/diluted standard seawater over ranges of salinity, temperature, and pressure to provide a data set for the reduction of *in-situ* measurements made using the most accurate modern instruments. This paper describes the empirical equations derived from this data and the details of the fitting procedure.

Of almost equal importance to the absolute accuracy of determinations made using the new scale is the fact that, providing that all users agree on the scale, it will produce a consistent basis for interinstitutional comparisons. A discussion of these problems, of the internal inconsistencies within past definitions of salinity, and of the variety of equations used to compute salinity has been given by Lewis and Perkin [1], who also list references to previous work. If future improvements in measurement techniques or fitting methods should make the present work obsolete, it is considered essential that no changes should be made until an entirely new Practical Salinity Scale can be accepted so that consistency in data comparison can be preserved.

The most important part of the present set of equations is based upon data supplied by three investigators in three different countries using different experimental apparatus, who have, in our judgement, provided one of the most consistent data set in existence for any purpose at a parts per million level of accuracy.

FITTING PROCEDURES

In order to simplify the data reduction process, the conductivity ratio is usually separated into three factors. Taking $C(S, T, P)$ as the *in-situ* electrical conductivity of seawater of practical salinity S, at temperature T and pressure P, the following notation is used.

$$R = \frac{C(S, T, P)}{C(35, 15, 0)}$$

$$R_P = \frac{C(S, T, P)}{C(S, T, 0)}$$

$$r_T = \frac{C(35, T, 0)}{C(35, 15, 0)}$$

$$R_T = \frac{C(S, T, 0)}{C(35, T, 0)}$$

$$R = R_P R_T r_T. \tag{1}$$

Temperature is in degrees Celsius (IPTS-68) and the units of pressure are decibars in accordance with oceanographic practice.

The quantity $C(35, 15, 0)$ has special status under the Practical Salinity Scale, being the conductivity of seawater of practical salinity 35‰ at 15°C which by definition has a conductivity equal to that of the standard KCl solution at that temperature.

In the reduction of *in-situ* data, r_T and R_P are computed from R, T, and P so that (1) can be used to compute R_T. Finally salinity is calculated from R_T and T; this equation includes, as a special case, the relationship between R_{15} and S which comprises the definition of the Practical Salinity Scale 1978.

It should be noted that the fits presented here are empirical, and no physical significance is attributed to the form of the equations. We have produced the best fit that we could using a minimum number of coefficients and reducing the residuals to levels where they are of no practical significance in terms of modern instrumentation.

Each of the factors r_T, $S = F(R_T, T)$, and the pressure conversion R_P will be dealt with in turn. Frequent reference will be made to data sets which are described and listed elsewhere in this volume by the investigators who produced them.

A. Fitting $r_T = C(35, T, 0)/C(35, 15, 0)$

The factorization given in (1) is designed so that r_T takes up most of the variance due to temperature in the reduction of conductivity data.

Two data sets were made available for fitting r_T. They are described in Dauphinee *et al.* [2] and Bradshaw and Schleicher [3] and consist of 34 and 36 points, respectively. Initially,

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The authors are with the Frozen Sea Research Group, Institute of Ocean Sciences, P. O. Box 6000, 9860 W. Saanich Rd., Sidney, B. C., Canada V8L 4B2.

TABLE I

DATA FITTED FOR $r_T = \dfrac{C(35, T, 0)}{C(35, 15, 0)}$ (3)

Temp. (°C)	r_T Bradshaw & Schleicher	r_T Dauphinee	r_T calc. (3)	$\Delta \times 10^5$ Bradshaw & Schleicher Exp.-Calc.	$\Delta \times 10^5$ Dauphinee Exp.-Calc.
−2	0.636939	0.636950	0.636944	−0.5	0.6
0	0.676604	0.676612	0.676610	−0.6	0.2
5	0.779561	0.779575	0.779566	−0.5	0.9
10	0.887527	0.887534	0.887529	−0.2	0.5
15	1	1	1	0	0
20	1.116495	1.116496	1.116493	0.2	0.3
25	1.236542	1.236541	1.236537	0.5	0.4
30	1.359688	1.359661	1.359679	0.9	−1.8
35	1.485495	1.485463	1.485478	1.7	−1.5

each data set was treated separately in order to generate values of r_T at the standard temperatures of −2, 0, 5, 10, 15, 20, 25, 30, and 35°C. This involved fitting r_T to a fourth degree polynomial in T, then dividing by the calculated value of r_{15} in order to satisfy $r_{15} \equiv 1$. This later step involved a change of less than 1 part in 10^6 or about 0.00004‰ in salinity equivalent. Both data sets had rms residuals of 1.1×10^{-5} in r_T and were combined at the standard temperatures mentioned above. Taking data at temperatures other than 15°C, a least square fit was made to the following form with weights equal to $|(T-15)|$ assigned to each point:

$$\frac{r_T - 1}{(T-15)} = c_0' + c_1'(T-15) + c_2'(T-15)^2 + c_3'(T-15)^3. \qquad (2)$$

All polynomial fits of this kind were done using the method of orthogonal polynomials [4] so as to minimize computer roundoff errors. Equation (2) was brought to the more familiar form of (3) below, and the coefficients were rounded so that the condition $r_{15} = 1$ was preserved to an accuracy of 8 decimal places.

$$r_T = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4, \quad -2 < T < 35°\text{C} \qquad (3)$$

$c_0 = 0.6766097$

$c_1 = 2.00564 \times 10^{-2}$

$c_2 = 1.104259 \times 10^{-4}$

$c_3 = -6.9698 \times 10^{-7}$

$c_4 = 1.0031 \times 10^{-9}$.

Table I lists the data generated from the two data sets, values of r_T calculated from (3) and the residuals. The rms difference for this fit is 0.82×10^{-5} in r_T which can be interpreted as the systematic disagreement between the two sets since the random errors have been smoothed in the initial fitting process. At 15°C, 35‰, 0.82×10^{-5} in r_T is equivalent to 0.00032‰ in salinity.

B. Fitting $S = F(R_T, T)$

This fit represents the final step in computing salinity and reduces to the defining equation for the Practical Salinity Scale when $T = 15$°C. As such it was divided, in the form developed by Dauphinee *et al.* (private communication 1979) into a term valid by itself at 15° and a correction term depending on temperature and R_T.

$$S(‰) = \sum_{j=0}^{5} a_j R_T^{j/2} + \frac{(T-15)}{1 + k(T-15)} \sum_{j=0}^{5} b_j R_T^{j/2}. \qquad (4)$$

It was expanded in powers of $R_T^{1/2}$ in order to better fit the almost second degree form of the relationship and was allowed to have a constant term in order to better fit the low salinity data; it is not valid below $S = 2$‰ ($R_{15} = 0.036786$).

Three data sets were utilized, those of Dauphinee *et al.* [2], of Poisson [5], and of Bradshaw and Schleicher [3]. In the first two data sets, readings of R_T were taken at various fixed temperatures for many salinities obtained by evaporating/diluting standard seawater P79 by weight with distilled deionized water. These two sets formed the body of data used for fitting. The third set was generated by measuring R_T as a function of temperature for various seawater samples characterized by particular values of R_{15}. Since S was determined from R_{15}, and not by diluting standard seawater, these data were used only as a check on the relationship arising from the data obtained by weighing. The polynomials in T used for the checking are given in (3). The Dauphinee *et al.* data set was accompanied by polynomials giving salinity by weight ratio as a function of R_T at fixed temperatures. In order to check the compatibility of these polynomials, comparisons were made at the (R_T, T) points at which both sets of polynomials were valid (Table IIA). In terms of the data as represented by these polynomials, agreement was within 0.0012‰ for all points of comparison and showed a standard deviation of $\approx$0.0004‰. The same comparison with Bradshaw and Schleicher's data was carried out on the polynomial derived from the data of Poisson with the result shown in Table IIB. Taking account of the slightly different method of comparison, the rms deviation of 0.0008‰ indicated that all the data sets are in good agreement and have com-

TABLE IIA
DIFFERENCE IN SALINITY EQUIVALENT ($^0/_{00} \times 10^4$) BETWEEN THE BRADSHAW AND THE SCHLEICHER AND DAUPHINEE *ET AL.* (B. AND S.-D.) DATA SETS FOR THE $S = F(R_T, T)$ FIT (5)*

R_{15} \ T°C	0	5	10	15	20	25	30	35
0.07	−3	−1	−1	0	−3	−2	−2	−1
0.20	1	−2	−1	0	−1	−1	0	−1
0.50	−1	−3	−2	0	0	2	2	0
0.77	2	1	1	0	−1	8	10	1
0.90	0	−7	−2	0	−1	2	1	1
1.00	4	−4	0	0	0	−1	−1	−2
1.09	3	−5	−1	0	−1	−9	−10	−5
1.17	12	5	2	0	2	−5	−3	−8
1.23	12	4	0	0	5	−5	−2	−9

* Their data was taken as represented by their sets of polynomials. R_{15} was converted to salinity using $S = F(R_{15})$ due to Dauphinee *et al.* so as to comapre the behavior at temperatures other than 15°C.

TABLE IIB
DIFFERENCE IN SALINITY ($^0/_{00} \times 10^4$) BETWEEN THE BRADSHAW AND SCHLEICHER POLYNOMIALS AND THE POLYNOMIAL REPRESENTING THE POISSON DATA*

R_{15} \ T°C	0	5	10	15	20	25	30	35
0.07								
0.20	−3	−8	−2	7	12	14	12	
0.50	−15	−25	−18	−7	1	2	−1	
0.77	−3	−4	−2	3	8	12	12	
0.90	−3	−5	−1	4	7	7	5	
1.00	0	0	0	0	0	0	0	
1.09	−3	0	−1	−5	−9	−11	−10	
1.17	12	15	6	−4	−9	−6	−0	
1.23								

* R_{15} was converted to salinity using P.S.S. '78.

parable standard deviations. The sets were therefore combined for the purposes of fitting into one set at $T = 15°$ and a second set at $T \neq 15°$. The range of data available for the fit was $2^0/_{00} < S < 42^0/_{00}$, $-2° < T < 35°$C.

The file containing the data at 15°C was fitted to the first polynomial in (4) using the method of orthogonal polynomials to determine the "a_j's." The fifth order was selected so as to minimize the standard deviation as represented by the sum of the squared residuals divided by the number of degrees of freedom in the fit [4]. The coefficients were rounded up to four decimal figures and no adjustment was necessary to satisfy the criterion

$$\sum_{j=0}^{5} a_j = 35.$$

At temperatures other than 15°, data points of

$$\left| \frac{S - \sum a_j R_T^{j/2}}{f(T)}, R_T \right|$$

were generated where

$$f(T) = \frac{(T-15)}{1 + k(T-15)}.$$

Fifth order fits were made to this form of the data for values of k in the neighborhood of $k = 0.0162$. The points were weighted with $\{f(T)\}^2$ in order to produce a more uniform distribution of salinity errors and the value of k along with its corresponding fifth order fit was chosen so as to minimize the sum of squared salinity errors in the $T \neq 15$ data set. These coefficients were rounded off to four decimal places. The second of these coefficients $b_2 = -0.006547$ was rounded up to -0.0066 in order to satisfy the criterion

$$\sum_{j=0}^{5} b_j = 0.$$

The completed fit is

$$S(^0/_{00}) = \sum_{j=0}^{5} a_j R_T^{j/2} + \frac{(T-15)}{1 + k(T-15)} \sum_{j=0}^{5} b_j R_T^{j/2}, \qquad (5)$$

$$k = 0.0162 \qquad 2^0/_{00} < S < 42^0/_{00}$$

$$-2° < T < 35°$$

$$\begin{aligned} a_0 &= 0.0080 & b_0 &= 0.0005 \\ a_1 &= -0.1692 & b_1 &= -0.0056 \\ a_2 &= 25.3851 & b_2 &= -0.0066 \\ a_3 &= 14.0941 & b_3 &= -0.0375 \\ a_4 &= -7.0261 & b_4 &= 0.0636 \\ a_5 &= 2.7081 & b_5 &= -0.0144. \end{aligned}$$

The residuals from this fit are given in Tables III and IV for Dauphinee *et al.* and Poisson, respectively. The rms residual is $0.66 \times 10^{-3}\,^0/_{00}$. For the 15°C data alone, the rms residual is $0.48 \times 10^{-3}\,^0/_{00}$.

C. Fitting $R_P = C(S, T, P)/C(S, T, 0)$

Data on the effect of pressure on the electrical conductivity of seawater was taken from Bradshaw and Schleicher [6] and a new data set due to the same authors [3]. The 1965 paper has been used by oceanographers for many years and is cited in virtually every algorithm for the conversion of *in-situ* data [1]. Operational experience, for example, Brown [7] has shown that *in-situ* calibrations produce data normally distributed about the values expected from their results. The new data set is more accurate and extensive but for the most part agrees with the 1965 publication; the two data sets were combined without weighting.

For oceanographic purposes, it was not necessary to use the full ranges of temperature, pressure, and salinity presented in their papers [3]. Bennett [8] gives the ranges of

TABLE III
RESIDUALS IN SALINITY EQUIVALENT (‰ × 10^4) FOR THE DATA DUE TO DAUPHINEE *ET AL.* (2) USED TO FIT (5)*

T°C R_T	$T < 0$°	0	5	10	15	20	25	30	35
0.00–0.05	−8		−1 −3	1 1	0, 2, 2	2	0	−8 −6	
0.05–0.10	−18			−4	−2, −2, −1, 0			−9	−18
0.10–0.15	−18		11	−7	−4, −4, −4, −1, −2, 0	0	−3	−11	
0.15–0.20		−17							
0.20–0.25		−14		−3	0, −2, 5, −1	2	−2	−10	−20
0.25–0.30	−8			−5	−4, −4,				
0.30–0.35		−14	−11	−3	−1, 4, 8, 0, −1	5	5	−5	
0.35–0.40	−1	−11		−7	−4, −1, 1				−15
0.40–0.45		−10		−4 −4	1, −2, −1	6	6		−7
0.45–0.50	4		−7	−3 −7	0, −4, 3			2	
0.50–0.55		−6	−5	−3 −2	2, 2, 1			5	
0.55–0.60	6				−4	8	9		1
0.60–0.65			−4	−4 −1 0	3, 3, 0, −3				
0.65–0.70	8	−5		−6 0	3, 7, 4, −1	9	9	7	
0.70–0.75			−1	−4	2, 5, 4	9			5
0.75–0.80	8	−4		−7	0, 4, 1, 2, 3,	8	9 2	6	6
0.80–0.85	7	−5	1	−1 −4	3, 6, 3, 4, 2, 5	6	7 6	3	4 4
0.85–0.90	6 5	−4 0	3	3 1 4 5 2	6, 4, 4, 6, −4 2	6 9 4	7 7 3	9 3	3
0.90–0.95	6	−3	4	1	−3, 0, 2, 2, 3 2, 0, 1		−1	0	4
	2	−2	−1 3	0 −14					
0.95–1.00	4 4	−6 −8 1	0 4 2	−5 −2 2 4	6, −5, 2, 7, 2, −3, 10,	3 3 −1 8 3	5 5 1 −1	5 −1 5	2 2 2 0
1.00–1.05	6 5	−6 −4	7	−1	−6, −2, 0, 4, −13, 4, −5, 0, −7, 0, −3, −2	−10 −4	0 2	−1	3 3 2
1.05–1.10	7	−5	5	1	−6, −5, −1, −5.2, −3, −3, 1, −5, −5, −3	−10	−2 −2 0	−3	−3
1.10–1.15	−4	−8	0	1	−2, 0, −2, −1, −4, −4	−4		−5	0
1.15–1.20		−14	−2	−1	−1, −4, −5, 4, −11, 0	−9	−5		−2

* Differences are experimental minus calculated.

pressure, temperature, and salinity which are relevant to oceanographic measurements. They are presented in Table V. This process of selecting the relevant data was necessary in order to generate a fit which did not require a large number of terms. A more extensive fit of all the data can be found in Bradshaw and Schleicher's more recent paper [3].

Comparing the overlapping section of the new and old data it was found that the old data at 35‰, 5°C and $P =$ 8015 dB, and 10 338 dB were at variance with the new data to the extent of ~0.007‰ in salinity equivalent. These two points were therefore dropped from the fitting procedure.

To combine the two data sets, the temperatures in the old set were converted to IPTS-68 by the equation due to Bennett [8]

$$T_{\mathrm{IPTS-68}} = T_{\mathrm{IPTS-48}}(1-4.88 \times 10^{-4}) + 5.80 \times 10^{-6} T_{\mathrm{IPTS-48}}^{2}$$

and the pressures in the old data set were converted, on the

TABLE IV
RESIDUALS IN SALINITY EQUIVALENT ($^0/_{00} \times 10^4$) FOR THE DATA DUE TO POISSON USED TO FIT (5)

R_T \ T°C	$T < 0$°	0	5	10	15	20	25	30	35
0.00–0.05									
0.05–0.10							−9		
0.10–0.15	−17	−1	−1	0 6	3	−11		−21	
0.15–0.20	−17		9 8	0	5, 10	−8 −3	−11	−18	
0.20–0.25		−5			2, 3, 1		−15	−12	
0.25–0.30	−13								
0.30–0.35		4	−1 6	11 9	0, 6	−14 0	−9 3	−10 −8	
0.35–0.40			0		−3, −3				
0.40–0.45	−9								
0.45–0.50		0	−1 10	2 9	0, −8	−5 −5	4 3	7 −4	
0.50–0.55			13 6		−6, −8				
0.55–0.60		10							
0.60–0.65	−6		15 1	14 15	−3, 3	28 4	−3 −15	6 3	
0.65–0.70			3 5		−3, −3				
0,70–0.75	1	−7	14 16	5 12	−7, −1	0 1	−2 −2	10 18	
0.75–0.80	−6								
0.80–0.85				11	−5, −7				
0.85–0.90		11	16 12	10	−8, −7	8 4	−8 5	6 9	
0.90–0.95		0			−4, −7 −2, −5, 0				
0.95-1.00			0		10	0	0	−3 3	
1.00–1.05				0 1			−2		
1.05-1.10		4	5	4	−4, 11	−5 −11	−6	3 8	
1.10–1.15		−2 2	5 8	2	14, 15 9, −6	−11	−6	13 8	
1.15–1.20				6	10, 16	−17	−10	12	

* Differences are experimental minus calculated.

TABLE V
MAXIMA OF THE RANGES OF PRESSURE (dB) OVER WHICH THE PRESSURE CORRECTION TO CONDUCTIVITY WAS FITTED

$S^0/_{00}$ \ T°C	$T < 0$	5	10	15	20	25	30
2							
14	1998	1998	1998	1998	1998	1998	1998
22	1998	1998	3996	1998	1998	1998	1998
31	1722	1722	1722	1722	1722	1722	
35	10,334	9988	3996	1998	1998	1998	1998
39	1722	1722	5162	5162	1722	1722	

advice of Bradshaw (private communication) by the equation

$$P_{\mathrm{TRUE}} = P_{\mathrm{OLD}}(0.999901 - 2.57 \times 10^{-7} P_{\mathrm{OLD}}).$$

No further adjustments were made to the data supplied.

For computation purposes R_P is usually given the form

$$R_P = 1 + \alpha \tag{6}$$

where $\alpha = f(R, T, P)$ is the fractional increase in conductivity due to pressure.

It is known that R_P is a similar function of pressure for all R and T so that it is reasonable to expect the pressure variable to be separable. The form

$$\alpha = \frac{P \times E(P)}{D(R, T)} \tag{7}$$

was assumed for fitting purposes.

The data was supplied as S, T, P, α, and it was necessary to generate R. (Equations (3) and (5) were used to do this.) An iterative fitting procedure was then set up whereby $E(P)$ was fitted by the method of orthogonal polynomials followed, cyclically, by an analysis of variance program which included a partial F test [9] to determine the relative significance of the variables to be included in $D(R, T)$. These two steps were applied alternately until the coefficients had converged. From the list of Const., R, T, RT, T^2, T^3, RT^2, $\sqrt{R}$, $\sqrt{RT}$, the combination chosen by the analysis of variance program was either Const., R, T, RT, T^2 or Const., $\sqrt{R}$, T, $\sqrt{RT}$,

TABLE VI
LARGEST RESIDUALS IN SALINITY EQUIVALENT ($^0/_{00} \times 10^3$) BETWEEN THE CALCULATED AND EXPERIMENTAL DATA FOR THE PRESSURE CORRECTION TO CONDUCTIVITY*

$S^0/_{00}$ \ T°C	$T < 0°$	5	10	15	20	25	30
2	3	3	3	3	3	3	3
14	2	3	3	2	2	2	2
22	0	−1	−2	−1	−1	−1	−1
31	−2	−2	−2	−2	−2	−1	
35	3	−3	−1	−1	−2	−1	0
39	4	3	4	2	0	1	

* A complete listing of the residuals is given in Appendix I. Data at $2^0/_{00}$ at pressures up to 1998 dB have been considered in addition to the data covering the oceanographic range of variables.

T^2 The former was chosen as the most convenient. The variables having been chosen, the analysis of variance program was replaced by a more accurate modified Gram-Schmidt method [1] developed by I. Barrodale at the University of Victoria, B.C. (private communication) and weighting was applied in order to make the deviations approximate their salinity equivalents. The fit obtained by this method was refined by Dauphinee and Ritchie (private communication) who perturbed each coefficient in turn while monitoring the sum of squared residuals in terms of the actual salinity errors. This system converged on (8) below giving an rms residual of $0.0013^0/_{00}$. The residuals are listed in Appendix I and the largest of these are given in Table VI with the pressures at which they occur given in Table VII.

$$R_P = 1 + \alpha$$

$$\alpha = \frac{P \times E(P)}{D(R, T)}, \qquad E(P) = A_1 + A_2 P + A_3 P^2 \tag{8}$$

$$A_1 = 2.070 \times 10^{-5}$$

$$A_2 = -6.370 \times 10^{-10}$$

$$A_3 = 3.989 \times 10^{-15}$$

$$D(R, T) = 1 + B_1 T + B_2 T^2 + B_3 R + B_4 RT$$

$$B_1 = 3.426 \times 10^{-2}$$

$$B_2 = 4.464 \times 10^{-4}$$

$$B_3 = 4.215 \times 10^{-1}$$

$$B_4 = -3.107 \times 10^{-3}$$

$$-2 \leqslant T \leqslant 30°\text{C}$$

$$2 \leqslant S \leqslant 39^0/_{00}$$

P(dB) see Table V.

Though not used to obtain the fit, data at $2^0/_{00}$ was found to agree with (8) to within 3 ppm at 2000 dB and it is listed along with the other data in the oceanographic range in Appendix I.

TABLE VII
THE PRESSURES (IN DECIBARS) AT WHICH THE LARGEST RESIDUALS LISTED IN TABLE VII OCCUR*

$S^0/_{00}$ \ T°C	$T < 0°$	5	10	15	20	25	30
2	1998	1998	1998	1998	1998	1998	
14	1998	1998	1998	1998	1998	1998	1998
22	1998	1998	3996	1998	1998	1998	1998
31	1722	1722	1722	1722	1722	1722	
35	9988	9988	3996	1998	1722	1998	1998
39	1722	1722	3443	1722	1722	1722	

* Except for the data at $39^0/_{00}$, the largest residuals occur near the highest pressures considered in the fi

CONCLUSIONS

Using newly generated data, a fit has been made giving the following algorithm for the calculation of salinity from data of the form:

$$R = \frac{C(S, T, P)}{C(35, 15, 0)}$$

T in °C (IPTS '68), P in decibars.

$$R_T = \frac{R}{R_P r_T}; \quad R_P = 1 + \frac{P \times (A_1 + A_2 P + A_3 P^2)}{1 + B_1 T + B_2 T^2 + B_3 R + B_4 RT}$$

$$r_T = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4$$

$$A_1 = 2.070 \times 10^{-5} \qquad B_1 = 3.426 \times 10^{-2}$$

$$A_2 = -6.370 \times 10^{-10} \qquad B_2 = 4.464 \times 10^{-4}$$

$$A_3 = 3.989 \times 10^{-15} \qquad B_3 = 4.215 \times 10^{-1}$$

$$B_4 = -3.107 \times 10^{-3}$$

$$c_0 = 6.766097 \times 10^{-1}$$

$$c_1 = 2.00564 \times 10^{-2}$$

$$c_2 = 1.104259 \times 10^{-4}$$

$$c_3 = -6.9698 \times 10^{-7}$$

$$c_4 = 1.0031 \times 10^{-9}$$

$$S = \sum_{j=0}^{5} a_j R_T^{\,j/2} + \frac{(T-15)}{1 + k(T-15)} \sum_{j=0}^{5} b_j R_T^{\,j/2}$$

$$a_0 = 0.0080 \qquad b_0 = 0.0005 \qquad k = 0.0162.$$

$$a_1 = -0.1692 \qquad b_1 = -0.0056$$

$$a_2 = 25.3851 \qquad b_2 = -0.0066$$

$$a_3 = 14.0941 \qquad b_3 = -0.0375$$

$$a_4 = -7.0261 \qquad b_4 = 0.0636$$

$$a_5 = 2.7081 \qquad b_5 = -0.0144$$

The rms deviations, in equivalent salinities of these fits are 0.0003‰, 0.0007‰, and 0.0013‰, respectively, for r_T, $S = F(R_T, T)$, and R_P. The overall standard deviation is estimated to be 0.0015‰ depending mainly on the pressure term. The residuals in this term are the same size as the errors expected from the accuracies obtained by *in-situ* pressure sensors. At atmospheric pressure ($P = 0$) and 15°C, the above algorithm reduces to the Practical Salinity Scale 1978.

It is hoped that the oceanographic community will find these equations useful and that standardization resulting from their general acceptance will allow more precise computations to proceed.

APPENDIX I

The following are the residuals over the oceanographic ranges of variables of the fit to the pressure effect on conductivity. The numbers in the column "DELTA SAL" are in salinity equivalents ‰ $\times 10^3$) and are the experimental values minus the calculated values. Data at 2‰ salinity have been included in the table although they were not used for fitting.

Salinity	Pressure	Temperature	DELTA SAL
31.000	1722.753	0.000	−2
35.000	1722.753	0.000	1
35.000	3445.354	0.000	−3
35.000	5167.802	0.000	−1
35.000	6890.097	0.000	−2
35.000	8612.240	0.000	1
35.000	10334.230	0.000	−2
39.000	1722.753	0.000	4
31.000	1722.753	4.998	−2
35.000	1722.753	4.998	−1
35.000	3445.354	4.998	0
35.000	5167.802	4.998	−2
35.000	6890.097	4.998	−1
39.000	1722.753	4.998	3
31.000	1722.753	9.996	−2
35.000	1722.753	9.996	0
35.000	3445.354	9.996	0
39.000	1722.753	9.996	3
39.000	3445.354	9.996	4
39.000	5167.802	9.996	4
31.000	1722.753	14.994	−2
35.000	1722.753	14.994	−1
39.000	1722.753	14.994	2
39.000	3445.354	14.994	1
39.000	5167.802	14.994	0
31.000	1722.753	19.993	−2
35.000	1722.753	19.993	−2
39.000	1722.753	19.993	0
31.000	1722.753	24.991	−1
35.000	1722.753	24.991	−1
39.000	1722.753	24.991	1
35.009	1.000	−1.850	1
35.009	59.000	−1.850	0
35.009	93.000	−1.850	−1
35.009	162.000	−1.850	0
35.009	1998.000	−1.850	−1
35.009	3998.000	−1.850	−2
35.009	5994.000	−1.850	0
35.009	7991.000	−1.850	2
35.009	9988.000	−1.850	3
35.009	1.000	4.250	0
35.009	59.000	4.250	0
35.009	93.000	4.250	0
35.009	162.000	4.250	0
35.009	1998.000	4.250	1
35.009	3996.000	4.250	1
35.009	5994.000	4.250	1
35.009	7991.000	4.250	1
35.009	9988.000	4.250	−3
35.009	1.000	10.000	0
35.009	59.090	10.000	0
35.009	93.000	10.000	0
35.009	162.000	10.000	0
35.009	1998.000	10.000	0
35.009	3996.000	10.000	−1
35.009	1.000	15.000	0
35.009	59.000	15.000	0
35.009	93.000	15.000	0
35.009	162.000	15.000	0
35.009	1998.000	15.000	−1
35.009	1.000	20.000	0
35.009	59.000	20.000	0
35.009	93.000	20.000	0
35.009	162.000	20.000	0
35.009	1998.000	20.000	−1
35.009	1.000	25.000	0
35.009	59.000	25.000	0
35.009	93.000	25.000	0
35.009	162.000	25.000	0
35.009	1998.000	25.000	−1
35.009	1.000	30.000	0
35.009	59.000	30.000	0
35.009	93.000	30.000	0
35.009	162.000	30.000	0
35.009	1998.000	30.000	0
22.066	1.000	−1.000	0
22.066	59.000	−1.000	0
22.066	93.000	−1.000	0
22.066	162.000	−1.000	0
22.066	1998.000	−1.000	0
22.066	1.000	5.000	0
22.066	59.000	5.000	0
22.066	93.000	5.000	0
22.066	162.000	5.000	0
22.066	1998.000	5.000	−1
22.066	1.000	10.000	0
22.066	59.000	10.000	0
22.066	93.000	10.000	0
22.066	162.000	10.000	0
22.066	1998.000	10.000	0
22.066	3996.000	10.000	−2
22.066	1.000	15.000	0
22.066	59.000	15.000	0
22.066	93.000	15.000	0
22.066	162.000	15.000	0
22.066	1998.000	15.000	−1
22.066	1.000	20.000	0
22.066	59.000	20.000	0
22.066	93.000	20.000	0
22.066	128.000	20.000	0
22.066	1998.000	20.000	−1
22.066	1.000	25.000	0
22.066	59.000	25.000	0
22.066	93.000	25.000	0
22.066	162.000	25.000	0
22.066	1998.000	25.000	−1
22.066	1.000	30.000	0
22.066	59.000	30.000	0
22.066	93.000	30.000	0
22.066	162.000	30.000	−1
22.066	1998.000	30.000	−1
14.052	1.000	−0.500	0
14.052	59.000	−0.500	0
14.052	93.000	−0.500	0
14.052	162.000	−0.500	0

Salinity	Pressure	Temperature	DELTA SAL
14.052	1998.000	−0.500	2
14.052	1.000	5.000	0
14.052	59.000	5.000	0
14.052	93.000	5.000	0
14.052	162.000	5.000	0
14.052	1998.000	5.000	3
14.052	1.000	10.000	0
14.052	59.000	10.000	0
14.052	93.000	10.000	0
14.052	162.000	10.000	0
14.052	1998.000	10.000	3
14.052	1.000	15.000	0
14.052	59.000	15.000	0
14.052	93.000	15.000	0
14.052	162.000	15.000	0
14.052	1998.000	15.000	2
14.052	1.000	20.000	0
14.052	59.000	20.000	0
14.052	93.000	20.000	0
14.052	162.000	20.000	0
14.052	1998.000	20.000	2
14.052	1.000	25.000	0
14.052	59.000	25.000	0
14.052	93.000	25.000	0
14.052	162.000	25.000	1
14.052	1998.000	25.000	2
14.052	1.000	30.000	0
14.052	59.000	30.000	0
14.052	93.000	30.000	0
14.052	162.000	30.000	0
14.052	1998.000	30.000	2
2.034	1.000	0.000	0
2.034	59.000	0.000	0
2.034	93.000	0.000	0
2.034	162.000	0.000	0
2.034	1998.000	0.000	3
2.034	1.000	5.000	0
2.034	59.000	5.000	0
2.034	93.000	5.000	0
2.034	162.000	5.000	0
2.034	1998.000	5.000	3
2.034	1.000	10.000	0
2.034	59.000	10.000	0
2.034	93.000	10.000	0
2.034	162.000	10.000	0
2.034	1998.000	10.000	3
2.034	1.000	15.000	0
2.034	59.000	15.000	0
2.034	93.000	15.000	0
2.034	162.000	15.000	0
2.034	1998.000	15.000	3
2.034	1.000	20.000	0
2.034	59.000	20.000	0
2.034	93.000	20.000	0
2.034	162.000	20.000	0
2.034	1998.000	30.000	3
2.034	1.000	25.000	0
2.034	59.000	25.000	0
2.034	93.000	25.000	0
2.034	162.000	25.000	0
2.034	1998.000	25.000	3
2.034	1.000	30.000	0
2.034	59.000	30.000	0
2.034	93.000	30.000	0
2.034	162.000	30.000	0
2.034	1998.000	30.000	3

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CONVERSION OF EXISTING DATA

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The Practical Salinity Scale 1978: conversion of existing data

E. L. LEWIS* and R. G. PERKIN*

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Abstract—Implementation of the recommendations to adopt the Practical Salinity Scale 1978 (PSS 78) as a world standard will require examination of existing archived salinity data with a view to its conversion into the new scale. This study gives the basis for conversion to the PSS 78 from six of the most commonly used current salinity algorithms. It will enable oceanographers to assess whether or not changes are significant in terms of their interests.

INTRODUCTION

THE PRACTICAL SALINITY SCALE 1978 (PSS 78) has been considered by the Joint Panel on Oceanographic Tables and Standards and has now been recommended by SCOR, ICES, and IAPSO as the scale in which to report future salinity data. It is the basis of the new international equation of state and presumably its use will become standard at most oceanographic institutes in the near future. The PSS 78 and its antecedents have been described by LEWIS (1980). This paper addresses the question of how to compare new data to those already existing in institutional archives. Oceanographers having full information regarding their old data tabulations, including the equations used to reduce electrical conductivities to salinities and values for the bottle samples used for calibration, should be able to use this study to assess the magnitude of the change caused by conversion to the new scale.

LEWIS and PERKIN (1978) listed salinity algorithms used to reduce conductivity–temperature–depth (CTD) measurements and from these, six have been selected as commonly in use at the present time. They are described in UNESCO (1966), PERKIN and WALKER (1972), FOFONOFF, HAYES and MILLARD (1974), BENNETT (1976), RIBE and HOWE (1975), and FEDOROV (1971). All the sets of equations are based on the data of COX, CULKIN and RILEY (1967) or BROWN and ALLENTOFT (1966), or both, using the relationship by BRADSHAW and SCHLEICHER (1965) for the pressure dependence of conductivity ratios. The International Oceanographic Tables (UNESCO, 1966), based on the data of COX *et al.* (1967), do not go below 10°C, making them unsuited by themselves for *in situ* CTD data reduction. All the other equation sets referred to are based either on the BROWN and ALLENTOFT data alone or on a marriage of the two data sets. The sets are the results of experiments on water masses with differing ionic ratios and, as has been discussed by LEWIS (1980), are fundamentally incompatible. This leaves considerable freedom for interpretation in joining the sets together and so variability in calculated salinities. The original equations

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* Frozen Sea Research Group, Institute of Ocean Sciences, 9860 West Saanich Road, Sidney, B.C. V8L 4B2, Canada.

supplied with the data sets have been used by some authors; others have used the original data, refitted to different functional forms. This was examined by LEWIS and PERKIN (1978), who also gave a general discussion of the philosophy of salinity determination and emphasized the need for a new scale to provide an unambiguous basis for inter-institutional data comparisons. The recommended solution is the PSS 1978; this set of equations is given in the Appendix; an issue of the *Journal of Oceanic Engineering* (Vol. 5, January 1980) was devoted to the topic. All the other algorithms can be obtained from the references given.

An additional complication in salinity calculations is the change in the definition of practical temperature in 1968 (Comité International des Poids et Mésures, 1969). Before that date the International Practical Temperature Scale (1948) was in common use and temperatures measured on that scale and on the following International Practical Temperature Scale (1968) will be represented as T_{48} and T_{68}, respectively. The distinction between the two scales has been mentioned by the originators of salinity algorithms to whom it is important and a number of conversion equations have been derived, which, although algebraically different, give essentially the same correction. We have used each relationship within the context of its own paper.

In what follows, it is particularly important to distinguish between the given measured quantities, which must be assumed errorless, and derived quantities that are an artifact of a particular algorithm or procedure. Measured quantities will be denoted by *italic* type, e.g. R, V, p, and derived quantities in normal type. Temperature and pressure are considered measured quantities because they are derived from a single measured electrical parameter by a fixed procedure, unlike salinity, which is calculated from both of them as well as electrical conductivity in a variety of ways. The conductivity of a particular parcel of water in the ocean of salinity S, temperature T and applied pressure p, is defined as $\mathrm{C}(\mathrm{S}, T, p)$ and a pertinent parameter is the ratio between the conductivity and that of some standard seawater solution at a given temperature and pressure. The usual standard has been the conductivity of 35‰ seawater at a temperature of 15°C at atmospheric pressure, $\mathrm{C}(35, \mathit{15}, \mathit{0})$. In the various authors' formulations, $\mathrm{C}(35, \mathit{15}_{48}, \mathit{0})$ or $\mathrm{C}(35, \mathit{15}_{68}, \mathit{0})$ may be the 'constant' used and allowance for this must be made when changing temperature scales. The point has been discussed by BENNETT (1976).

Methods of applying corrections to old data depend not only on the equations used, but on the technique used to calibrate the instrument. The two common calibration practices are not equivalent in all regards and give different biases to the data sets to which they are applied. These are systematic and can be related to each other.

CALIBRATION TECHNIQUES FOR *IN SITU* MEASUREMENTS

The calibration of the *in situ* machine first involves placing limits of accuracy on temperature and pressure measurements, because these are independent variables. The *in situ* machine also provides an output voltage, V, or some other electrical analog, proportional to the ratio between the conductivity of the water(at its *in situ* temperature T^{i} and pressure p) and $\mathrm{C}(35, \mathit{15}, \mathit{0})$ thus:

$$\mathrm{R} = \frac{\mathrm{C}(\mathrm{S}, T^{\mathrm{i}}, p)}{\mathrm{C}(35, \mathit{15}, \mathit{0})} = \mathrm{K} \,.\, V(\mathrm{S}, T^{\mathrm{i}}, p), \qquad (1)$$

where K is the cell constant, a function of the geometry of the cell. Next, a water sample collected at the same depth, location, and time the *in situ* reading was made is analysed in the bench salinometer to determine R_T, the ratio of the sample conductivity at temperature T to that of the standard seawater at the same temperature:

$$R_T = C(S, T, 0)/C(35, T, 0). \tag{2}$$

In some bench salinometers the standard seawater and the sample are run successively into a conductivity cell within a constant temperature bath so that T of equation (2) is known and R_T is determined directly. In others, without thermostatic control, the temperature of the sample must still be measured, but it is specified that this temperature and that of the standard seawater must not differ by more than 3°C. Temperature differences up to this size are compensated for by an electronic network designed with knowledge of the temperature coefficient of the standard seawater,

$$r_T = C(35, T, 0)/C(35, 15, 0). \tag{3}$$

The final piece of information required to complete the calibration process is the pressure dependence of the conductivity ratio:

$$R_p = \frac{C(S, T^i, p)}{C(S, T^i, 0)} = [1 + P(R, T^i, p)], \tag{4}$$

which allows connection between the *in situ* ratio and that which would have been measured on a bench salinometer at the same temperature. From (1), (2), (3), and (4),

$$R = R_p R_T^i r_T^i. \tag{5}$$

R_T^i is solved for by an iterative process from the value of R_T measured by the bench salinometer (at temperature T) from knowledge of the form of its temperature dependence. As r_T and R_p are given functions, part of the salinity algorithm, R follows from equation (5) by a process of successive approximation. Thus the cell constant K is determined as a correction ΔK applied to the previous value. Once this has been done R can be considered as a measured quantity, R, and subsequent values for R_T^i are calculated from (5). The final step is to calculate salinity from an equation of the form

$$S = G(R_T, T), \tag{6}$$

which in practice determines 'salinity' for the scale. Formally, the definition of salinity is usually equation (6) for $T = 15$°C or its equivalent (see Appendix for the definition of 'practical salinity'). Differences between salinities calculated from the various algorithms involve differences in data bases and/or fittings for the forms of R_T, r_T, and R_p as well as the form of (6). This can be explicitly expressed as:

$$\begin{aligned} S &= F(R, T, p) \\ &= G(R/R_p r_T, T) \text{ for } \textit{in situ} \text{ readings} \\ &= G(R_T, T) \text{ when } p = 0 \text{ (bench salinometer).} \end{aligned} \tag{7}$$

The above method of *in situ* CTD calibration and use will be called the ΔK technique. However, many investigators, particularly those concerned with narrow salinity ranges, use an additive correction to salinity, the ΔS method. Salinities are calculated directly from the bench salinometer and *in situ* readings, R_T, and (R, T^i, p), respectively, using equation (7); the difference between these values constitutes ΔS, which is then added algebraically to all values of salinity calculated from subsequent *in situ* readings. As will be shown later, this common procedure is only exact at the salinity at which ΔS is calculated. It would have been better to apply a correction proportional to salinity rather than a fixed value.

The conversion of data that have been reduced using any of the six listed algorithms by either the ΔK or ΔS method to the PSS 78 will now be investigated in detail.

INSPECTION AND TESTING OF EXISTING DATA SETS

In the following discussion, salinities resulting from existing calculations, including the appropriate calibration corrections, will be denoted by S and corresponding practical salinities on the PSS 78 by S'. The actual quantity measured by the *in situ* instrument is a voltage or equivalent, which should be errorless and independent of any calibration process or salinity scale. Thus from (7) (dropping T and p from the notation as understood)

$$S = F(KV), \qquad S' = F'(K'V),$$

where K and K' have been individually calculated on each scale, as described in the preceding section, by using $S = G(R_T)$ and $S' = G'(R_T)$ on the same bottle sample. S is measured in ‰, but this symbol has been omitted in the following discussion. Thus the change in salinity when converting to the PSS 78 is, from Taylor's expansion

$$\begin{aligned} S' - S &= F'(K'V) - F(KV) \\ &= F'(K'V) - F(K'V) - (K - K')V \cdot \frac{\partial F}{\partial R} \\ &= \Delta F - (1 - K'/K)R\frac{\partial F}{\partial R}. \end{aligned}$$

It is seen that ΔF is the component of the salinity difference due to changing algorithms. Now $R(\partial F/\partial R)$ can be written as $\delta S/(\delta R/R)$ and $\delta R/R$ is almost independent of temperature and pressure for a given δS. Thus, to the accuracy required, $\delta S/(\delta R/R)$ is independent of temperature and pressure and it can be demonstrated that it can be fitted to a quadratic,

$$R(\partial F/\partial R) = aS + bS^2,$$

to within small limits. The values of the constants a and b are 1.0683 and 0.00156 with an r.m.s. deviation in $R(\partial F/\partial R)$ of 6×10^{-3}. Thus

$$S' - S = \Delta F - (1 - K'/K)(aS + bS^2). \tag{8}$$

Taking the case of the bottle sample collected at specified values of V, T', and p and analysed on the bench to give R_T and T, (7) and (8) give

$$S' - S = \Delta G_B = \Delta F_B - (1 - K'/K)(aS_B + bS_B^2), \tag{9}$$

where the subscript B has been used to distinguish the bottle sample values. It is seen that ΔG_B is the salinity difference due to changing the algorithm used for the bench salinometer readings. Now ΔG_B and ΔF_B are known directly, hence $(1 - K'/K)$ can be calculated from (9) and applied to (8) to calculate $S' - S$ for any values of V, T', and p.

Table 1 lists the algorithms for which ΔF and ΔG corrections have been calculated along with their ranges of validity and information about conversion of temperature scales. A first estimate of the magnitude of the corrections is seen in Table 2 where ΔG_B has been listed for the International Tables. As the remaining five referenced sets of algorithms are close to

Table 1. Review of the salinity algorithms considered, giving ranges of validity, and conversions needed for comparison with the Practical Salinity Scale 1978

Salinity algorithm*	Ranges			Conversions		Reference
	Pressure (dbar)†	Temperature (°C)	Salinity	Temperature‡	Conductivity	Table No.
Cox, Culkin and Riley (1967) (International Tables)	0	10 to 30 14 to 29*	4 to 42	—	—	2
Fofonoff, Hayes and Millard (1974)	0 to 10,000	0 to 35 14 to 29*	4 to 42	$T_{68} \rightarrow T_{48}$	$R^{48} = 1.000106R^{68}$	3
Perkin and Walker (1972)	0 to 1,700	Freezing to 20	4 to 40	$T_{68} \rightarrow T_{48}$	$C^{48} = 42.9284R^{68}$	4
Bennett (1976)	0 to 10,000	Freezing to 35	4 to 42	—	—	5
Ribe and Howe (1975)§	0 to 7,000	0 to 30	20 to 40	—	—	6
Fedorov (1971)§	0 to 2,000	0 to 30	33 to 37	—	—	7

* Range of data. Fofonoff *et al.* (1974) state that their algorithm works at temperatures below 14°C (see Table 3).

† 1 dbar = 10 kilopascals.

‡ $T_{48} = T_{68}(1.000488 - 5.80 \times 10^{-6} T_{68})$.

§ Conversion of temperature scale omitted because of unclear or missing notification. It is thought that most investigators will have used the uncorrected formulation given here.

Table 2. The salinity difference in ‰ $\times 10^3$ calculated by the PSS 78 minus that given by the International Tables starting from the same measured values of R_T and T

Pressure, 0 dbar

Temperature, °C \ Salinity, ppt	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
34	+23	+29	+39	+44	+45	+41	+35	+28	+21	+15	+9	+6	+3	+2	+1	+1	+0	−1	−2	−5	−8
32	+22	+28	+38	+43	+44	+40	+35	+28	+21	+15	+10	+6	+4	+3	+2	+1	+0	−1	−3	−6	−10
30	+22	+27	+37	+42	+43	+40	+34	+28	+21	+15	+11	+7	+5	+3	+2	+2	+1	−1	−3	−6	−10
28	+21	+26	+36	+41	+42	+39	+34	+27	+21	+15	+11	+7	+5	+4	+3	+2	+1	−1	−3	−7	−11
26	+21	+25	+35	+40	+41	+38	+33	+27	+21	+16	+11	+8	+6	+4	+3	+2	+1	−1	−4	−7	−11
24	+21	+25	+34	+39	+40	+38	+33	+27	+21	+16	+12	+8	+6	+5	+3	+2	+1	−1	−4	−7	−12
22	+20	+24	+33	+39	+40	+37	+33	+27	+21	+16	+12	+9	+6	+5	+4	+2	+1	−1	−4	−7	−12
20	+20	+23	+32	+38	+39	+37	+32	+27	+21	+16	+12	+9	+7	+5	+4	+3	+1	−1	−4	−8	−11
18	+20	+23	+32	+38	+39	+37	+33	+27	+22	+17	+13	+10	+7	+6	+4	+3	+1	−1	−4	−8	−11
16	+20	+23	+32	+38	+39	+37	+33	+28	+23	+18	+14	+10	+8	+6	+5	+3	+1	−1	−4	−8	−11
14	+20	+23	+32	+38	+39	+38	+34	+29	+23	+19	+15	+11	+9	+7	+5	+3	+1	−1	−4	−8	−11
12	+20	+23	+32	+38	+40	+39	+35	+30	+25	+20	+16	+13	+10	+8	+6	+4	+1	−1	−4	−8	−11
10	+21	+24	+33	+39	+41	+40	+36	+32	+27	+22	+18	+14	+11	+9	+6	+4	+1	−2	−5	−8	−11
8	+21	+25	+34	+41	+43	+42	+39	+34	+29	+24	+20	+16	+13	+10	+7	+4	+2	−2	−5	−8	−11
6	+22	+26	+36	+43	+46	+45	+42	+37	+32	+27	+23	+19	+15	+12	+8	+5	+2	−2	−6	−9	−12
4	+24	+28	+39	+46	+49	+49	+46	+41	+36	+31	+27	+22	+18	+14	+10	+6	+2	−2	−6	−10	−13
2	+25	+31	+42	+50	+54	+53	+51	+47	+41	+36	+31	+26	+21	+17	+12	+7	+2	−2	−7	−11	−14
0	+27	+34	+46	+55	+59	+59	+57	+53	+48	+42	+37	+31	+26	+20	+15	+9	+3	−3	−9	−14	−17
−2	+29	+38	+51	+61	+66	+67	+65	+61	+56	+50	+44	+37	+31	+24	+18	+11	+4	−4	−10	−16	−20

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* Dashed line encloses the region of validity of the equations as given in Table 1.

the International Tables over that part of their range (two of them are identical). Table 2 is a good guide to what is to follow. The values of ΔG_B are mostly the result of ionic ratio differences between the waters giving rise to the two data sets used and this has been discussed by LEWIS (1980). Both data sets have the IAPSO standard seawater in common which in the past, with few exceptions, has been good as a conductivity standard within ± 0.002 salinity (POISSON, DAUPHINEE, ROSS and CULKIN, 1978) and at $S = 35$, $\Delta G \sim 0.0$ independent of temperature.

Tables 3 to 7 give the salinity differences, ΔF, at various pressures between the PSS 78 and the five remaining salinity algorithms calculated from the same measured values. ΔG_B is tabulated in each case for three laboratory temperatures, 16, 20, and 24°C. Except in extreme cases, linear interpolation between values in the tables is sufficient to give an accuracy of ± 2 ppm for $S' - S$. The use of the tables is best described by giving an example.

Consider a profile where a bottle sample has been taken at 1000 dbar pressure and temperature 0°C. The sample has been analysed aboard ship at a temperature of 20°C to give a salinity of 36 by the algorithm due to FOFONOFF *et al.* (1974), which has then been used to compute profile salinities corrected by the ΔK method. At 20-m depth in the profile the salinity so computed is 28 at a temperature of 4°C. What salinity would have been computed if PSS 78 had been used throughout?

Referring to Table 3 (FOFONOFF *et al.*, 1974), the parameters for the bottle sample ($T = 0°C$, $S = 36$, $p = 1000$ dbar) give $\Delta G_B = -1 \times 10^{-3}$, $\Delta F_B = -13 \times 10^{-3}$, and $aS + bS^2 = 40$. Thus (9) gives

$$(1 - K'/K) = (-13 + 1)10^{-3}/40 = -30 \times 10^{-5}.$$

Referring to Table 3 (0 dbar) for the profile point of interest ($T = 4°C$, $S = 28‰$), $\Delta F = 15 \times 10^{-3}$ and $aS + bS^2 = 31$. Equation (8) then gives

$$S' - S = 15 \times 10^{-3} + 30 \times 10^{-5} \times 31 = 24 \times 10^{-3}.$$

Therefore, salinities at this point of the profile would have been 0.024 higher if PSS 78 had been used.

The ΔS calibration technique is differently formulated: the *in situ* salinity is forced to agree with the corresponding bottle sample value at any point in the profile:

$$S = F(R) + \Delta S$$

where

$$\Delta S = G_B - F(R_B).$$

Using the same measured values but the PSS 78

$$S' = F'(R) + G'_B - F'(R_B)$$

where R is a measured value. Thus:

$$S' - S = F'(R) - F(R) - [F'(R_B) - F(R_B)] + G'_B - G_B,$$

or

$$S' - S = \Delta F - \Delta F_B + \Delta G_B. \tag{10}$$

Taking the same example, ΔG_B, ΔF_B, and ΔF remain unchanged at -1×10^{-3}, -13×10^{-3}, and 15×10^{-3} respectively. From (10)

$$S' - S = 15 + 13 - 1 = 27 \times 10^{-3}.$$

Table 3. Values for ΔF (‰ × 10^3), the salinity difference between the PSS 78 and Fofonoff et al. (1974) *calculated from the same measured values at pressures of 0, 1000, 2000, and 5000 dbar*

Pressure, 0 dbar

Temperature, °C	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
34	+22	+28	+38	+43	+43	+39	+33	+26	+18	+12	+6	+2	+0	−2	−3	−4	−5	−6	−8	−11	−15
32	+22	+28	+38	+43	+44	+40	+34	+28	+21	+15	+10	+6	+4	+2	+2	+1	+0	−1	−3	−6	−10
30	+22	+27	+37	+43	+44	+41	+35	+29	+22	+17	+12	+9	+6	+5	+4	+4	+3	+2	−1	−4	−8
28	+22	+26	+36	+42	+43	+40	+35	+29	+23	+17	+13	+10	+8	+7	+6	+5	+4	+3	+1	−3	−7
26	+21	+26	+35	+41	+42	+40	+35	+29	+23	+18	+13	+10	+8	+7	+6	+6	+5	+3	+0	−3	−7
24	+21	+25	+34	+40	+41	+39	+34	+28	+23	+18	+14	+10	+8	+7	+6	+5	+4	+2	+0	−4	−8
22	+20	+24	+33	+39	+40	+38	+34	+28	+22	+17	+13	+10	+8	+7	+6	+5	+3	+1	−1	−5	−9
20	+20	+24	+33	+38	+40	+37	+33	+28	+22	+17	+13	+10	+8	+6	+5	+4	+2	+0	−3	−6	−10
18	+20	+23	+32	+38	+39	+37	+33	+27	+22	+17	+13	+10	+8	+6	+5	+3	+1	−1	−4	−7	−11
16	+20	+23	+32	+38	+39	+37	+33	+28	+23	+18	+14	+10	+8	+6	+5	+3	+1	−1	−4	−7	−11
14	+20	+23	+32	+38	+39	+38	+34	+29	+24	+19	+15	+11	+9	+7	+5	+3	+1	−1	−4	−7	−11
12	+20	+23	+32	+38	+40	+39	+35	+30	+25	+20	+16	+13	+10	+8	+6	+4	+2	−1	−4	−7	−10
10	+21	+24	+33	+40	+42	+40	+37	+32	+27	+23	+19	+15	+12	+10	+8	+5	+3	+0	−3	−6	−9
8	+22	+25	+35	+41	+44	+43	+40	+35	+30	+26	+21	+18	+15	+12	+9	+7	+4	+1	−3	−6	−8
6	+23	+27	+37	+44	+46	+46	+43	+38	+34	+29	+24	+21	+17	+14	+11	+8	+4	+1	−3	−6	−8
4	+24	+29	+39	+46	+50	+49	+46	+42	+37	+32	+28	+23	+19	+15	+12	+8	+4	+0	−4	−8	−11
2	+25	+31	+42	+50	+53	+53	+50	+46	+41	+35	+30	+25	+20	+15	+11	+6	+1	−4	−9	−13	−16
0	+27	+33	+44	+53	+57	+56	+54	+49	+43	+37	+31	+25	+19	+13	+7	+1	−6	−12	−18	−24	−28
−2	+28	+35	+47	+56	+60	+59	+56	+51	+45	+37	+30	+23	+15	+7	−1	−9	−18	−26	−34	−42	−47

Salinity, ppt

Table 3—continued

Temperature, °C	1000 dbar						2000 dbar						5000 dbar					
Salinity, ppt	30	32	34	36	38	40	30	32	34	36	38	40	30	32	34	36	38	40
36																		
34																		
32	−5	−6	−7	−9	−12	−16	−10	−11	−13	−16	−20	−24	−17	−19	−22	−26	−31	−38
30	+1	+0	−1	−3	−6	−10	−1	−3	−4	−7	−10	−15	−4	−6	−8	−12	−17	−23
28	+5	+4	+3	+1	−2	−6	+4	+3	+1	−1	−5	−9	+5	+3	+1	−2	−7	−13
26	+7	+6	+4	+2	−1	−5	+7	+6	+4	+2	−2	−6	+11	+9	+7	+3	−2	−8
24	+8	+6	+5	+3	−1	−5	+9	+8	+6	+3	−1	−6	+14	+12	+9	+6	+1	−6
22	+8	+6	+5	+2	−1	−6	+9	+8	+6	+3	−1	−6	+15	+13	+10	+6	+1	−6
20	+7	+6	+4	+1	−2	−7	+9	+7	+5	+2	−2	−7	+15	+13	+10	+5	+0	−7
18	+7	+5	+3	+0	−4	−8	+9	+7	+4	+1	−4	−9	+14	+12	+8	+4	−2	−9
16	+7	+5	+2	−1	−5	−9	+8	+6	+3	+0	−5	−10	+14	+11	+7	+2	−4	−12
14	+7	+5	+2	−1	−5	−10	+8	+6	+3	−1	−6	−12	+13	+10	+6	+1	−6	−14
12	+8	+5	+2	−1	−5	−10	+9	+6	+3	−1	−7	−12	+14	+10	+6	+0	−7	−15
10	+9	+6	+3	−1	−5	−10	+10	+7	+3	−1	−7	−13	+15	+11	+6	+0	−8	−16
8	+10	+7	+4	+0	−5	−10	+12	+8	+4	−1	−7	−13	+16	+12	+7	+0	−8	−18
6	+12	+8	+4	+0	−5	−10	+13	+9	+4	−1	−7	−14	+18	+13	+7	+0	−9	−19
4	+13	+9	+4	−2	−7	−13	+15	+10	+4	−2	−9	−16	+19	+14	+7	−2	−11	−22
2	+13	+7	+1	−5	−12	−18	+14	+8	+2	−6	−14	−22	+19	+13	+4	−5	−16	−28
0	+9	+2	−5	−13	−21	−29	+11	+4	−4	−13	−23	−33	+16	+8	−2	−13	−26	−40
−2	+1	−8	−17	−27	−37	−47	+4	−6	−16	−27	−39	−51	+9	−2	−14	−28	−43	−59
−4																		

Salinity, ppt	ΔG$_a$ 16 °C	20 °C	24 °C
42	−11	−11	−12
40	−8	−8	−7
38	−4	−4	−4
36	−1	−1	−1
34	+1	+1	+1
32	+3	+3	+2
30	+5	+4	+3
28	+6	+5	+5
26	+8	+7	+6
24	+10	+9	+8
22	+14	+12	+12
20	+18	+16	+16
18	+23	+21	+21
16	+28	+27	+27
14	+33	+32	+33
12	+37	+37	+38
10	+39	+39	+40
8	+38	+38	+39
6	+32	+32	+34
4	+23	+23	+25
2	+20	+20	+21

ΔG$_a$ at the lower right of Tables 3 to 7 gives the calculated change in bottle sample salinities used for calibration purposes. See text for discussion and method of use. Dashed line encloses the region of validity of the equations as given in Table 1.

Table 4. *Values for* ΔF (‰ × 10³), *the salinity difference between the PSS 78 and* Perkin *and* Walker (1972) *calculated from the same measured values at pressures of* 0, 500, 1000, *and* 2000 *dbar*

Pressure, 0 dbar

Temperature, °C \ Salinity, ppt	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
34	+46	−9	−28	−32	−32	−34	−37	−38	−36	−31	−26	−20	−13	−7	+0	+7	+14	+23	+34	+49	+68
32	+49	−4	−22	−25	−24	−25	−28	−29	−27	−23	−19	−14	−9	−4	+1	+6	+11	+17	+26	+38	+55
30	+52	+0	−16	−19	−17	−17	−20	−22	−20	−17	−13	−9	−5	−2	+1	+4	+8	+12	+19	+28	+43
28	+54	+3	−12	−14	−12	−12	−14	−16	−15	−12	−9	−6	−3	+0	+2	+3	+5	+8	+13	+21	+33
26	+55	+6	−9	−10	−7	−7	−10	−12	−11	−8	−6	−3	−1	+1	+2	+3	+3	+5	+8	+14	+25
24	+56	+7	−6	−7	−4	−4	−6	−8	−7	−5	−3	−1	+0	+1	+2	+2	+2	+2	+5	+9	+18
22	+56	+8	−5	−5	−2	−1	−4	−6	−5	−3	−2	+0	+1	+2	+2	+1	+1	+1	+2	+6	+13
20	+56	+9	−4	−4	+0	+0	−2	−4	−4	−2	−1	+1	+2	+2	+2	+1	+0	+0	+0	+3	+10
18	+56	+9	−3	−3	+1	+1	−1	−3	−3	−2	+0	+1	+2	+2	+2	+1	+0	+0	+0	+2	+7
16	+55	+9	−3	−3	+1	+2	−1	−3	−3	−2	+0	+1	+2	+2	+2	+2	+1	+0	+0	+1	+5
14	+55	+8	−4	−3	+1	+2	−1	−3	−3	−2	−1	+0	+1	+2	+2	+2	+1	+1	+0	+1	+4
12	+54	+8	−4	−4	+0	+1	−1	−4	−4	−3	−1	+0	+1	+2	+2	+3	+2	+2	+1	+1	+4
10	+53	+7	−5	−4	−1	+1	−2	−4	−4	−3	−2	−1	+0	+1	+2	+3	+3	+3	+2	+2	+3
8	+52	+6	−6	−5	−1	+0	−2	−5	−5	−4	−3	−2	−1	+1	+2	+3	+4	+3	+2	+1	+1
6	+50	+5	−7	−6	−2	−1	−3	−6	−6	−5	−5	−3	−2	+0	+1	+3	+4	+3	+2	+0	−1
4	+49	+5	−7	−6	−2	−1	−3	−6	−7	−7	−6	−5	−4	−2	+0	+2	+2	+2	+0	−2	−6
2	+48	+4	−7	−6	−2	−1	−4	−7	−8	−8	−8	−7	−6	−4	−2	−1	+0	−1	−3	−8	−13
0	+51	+8	−4	−2	+2	+3	+0	−3	−5	−6	−6	−6	−6	−4	−3	−1	−1	−3	−7	−13	−21
−2	+70	+27	+16	+18	+22	+23	+20	+16	+14	+12	+11	+10	+10	+10	+11	+12	+11	+8	+2	−6	−17

Table 4— continued

Temperature, °C	500 dbar						1000 dba:						2000 dbar					
0	30	32	34	36	38	40	30	32	34	36	38	40	30	32	34	36	38	40
36																		
34																		
32	−4	+0	+5	+10	+18	+29	−5	−1	+3	+8	+15	+26	+3	+7	+10	+15	+22	+32
30	−3	−1	+2	+5	+11	+20	−4	−2	+0	+3	+8	+16	+4	+6	+8	+11	+15	+23
28	−3	−2	−1	+1	+5	+12	−4	−4	−3	−1	+2	+8	+5	+6	+6	+7	+10	+16
26	−3	−3	−3	−2	+0	+5	−4	−4	−5	−5	−3	+2	+6	+5	+5	+5	+6	+10
24	−3	−4	−5	−5	−4	+0	−4	−5	−6	−7	−7	−3	+7	+6	+4	+3	+3	+6
22	−3	−4	−6	−7	−6	−3	−4	−6	−7	−9	−9	−7	+8	+6	+4	+2	+1	+3
20	−3	−5	−6	−8	−8	−6	−4	−6	−8	−10	−11	−9	+8	+6	+4	+2	+1	+2
18	−3	−5	−7	−8	−9	−8	−4	−6	−8	−10	−12	−11	+9	+7	+5	+3	+1	+1
16	−4	−5	−6	−8	−9	−9	−4	−6	−8	−10	−12	−12	+10	+8	+6	+4	+2	+1
14	−4	−5	−6	−8	−9	−9	−4	−6	−7	−10	−11	−12	+11	+10	+8	+5	+3	+2
12	−4	−4	−6	−7	−8	−9	−4	−5	−7	−9	−11	−12	+12	+11	+9	+7	+5	+4
10	−4	−4	−5	−6	−8	−9	−4	−5	−6	−8	−10	−12	+12	+12	+11	+9	+7	+5
8	−5	−4	−5	−6	−8	−10	−5	−5	−6	−8	−10	−13	+13	+13	+12	+10	+8	+6
6	−6	−5	−5	−7	−9	−11	−6	−6	−7	−8	−11	−14	+12	+13	+12	+11	+8	+5
4	−8	−7	−7	−8	−11	−15	−8	−8	−9	−10	−14	−18	+11	+12	+12	+10	+7	+3
2	−11	−10	−10	−12	−16	−21	−12	−11	−12	−14	−18	−24	+9	+10	+9	+8	+4	−2
0	−12	−12	−12	−15	−20	−27	−13	−13	−14	−17	−22	−30	+8	+9	+8	+6	+1	−7
−2	+1	+0	−1	−5	−12	−21	−1	−1	−4	−8	−15	−25	+21	+21	+20	+16	+9	+0
−4																		

Salinity, ppt

Salinity, ppt	16	20	24
42	+6	+10	+16
40	+1	+3	+7
38	+0	+0	+2
36	+0	+0	+0
34	+1	+0	+0
32	+2	+1	+0
30	+2	+2	+0
28	+2	+2	+0
26	+2	+2	−1
24	+1	+1	−3
22	+0	−1	−4
20	−2	−2	−7
18	−3	−4	−9
16	−3	−4	−9
14	−1	−2	−7
12	+2	+0	−4
10	+1	+0	−5
8	−3	−3	−7
6	−3	−4	−7
4	+[illegible]	+9	+7
2	+55	+56	+56

°C

ΔG_B

See footnote to Table 3.

Table 5. Values for ΔF (‰ × 10^3), the salinity difference between the PSS 78 and BENNETT *(1976) calculated from the same measured values at pressures of 0, 1000, 2000, and 5000 dbar*

Pressure, 0 dbar

Temperature, °C	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
34	+18	+20	+28	+31	+31	+27	+21	+13	+6	+0	−6	−11	−15	−17	−20	−22	−24	−26	−28	−30	−32
32	+20	+23	+32	+37	+37	+35	+30	+23	+17	+12	+7	+3	+0	−2	−3	−5	−6	−8	−10	−11	−13
30	+20	+25	+34	+40	+41	+39	+35	+29	+24	+19	+14	+11	+9	+7	+6	+4	+3	+2	+0	−2	−3
28	+21	+25	+35	+41	+43	+41	+37	+32	+27	+22	+18	+15	+12	+11	+9	+8	+7	+5	+3	+1	−1
26	+21	+25	+35	+42	+43	+42	+38	+33	+27	+23	+19	+15	+13	+11	+10	+9	+7	+5	+3	+1	−2
24	+21	+25	+35	+41	+43	+41	+37	+32	+27	+22	+18	+15	+12	+10	+9	+7	+5	+3	+1	−2	−5
22	+21	+25	+34	+40	+42	+40	+36	+31	+26	+21	+17	+14	+11	+9	+7	+5	+3	+1	−2	−5	−8
20	+21	+24	+34	+40	+41	+39	+35	+30	+25	+20	+16	+12	+10	+7	+6	+4	+2	−1	−4	−7	−10
18	+20	+24	+33	+39	+40	+38	+34	+29	+24	+19	+15	+11	+9	+7	+5	+3	+1	−2	−5	−8	−11
16	+20	+23	+32	+38	+39	+38	+34	+28	+23	+18	+14	+11	+8	+6	+5	+3	+1	−2	−5	−8	−11
14	+20	+23	+32	+37	+39	+37	+33	+28	+23	+18	+14	+11	+8	+7	+5	+3	+1	−1	−4	−7	−10
12	+20	+22	+31	+37	+38	+36	+32	+27	+22	+18	+14	+11	+9	+7	+6	+4	+2	+0	−2	−6	−9
10	+20	+22	+30	+36	+38	+36	+32	+27	+22	+18	+14	+11	+9	+7	+6	+5	+3	+1	−2	−5	−8
8	+20	+22	+30	+35	+37	+35	+31	+26	+21	+17	+13	+10	+8	+7	+6	+4	+3	+1	−2	−5	−8
6	+19	+21	+29	+35	+36	+34	+30	+25	+20	+16	+12	+9	+7	+6	+4	+3	+1	−1	−3	−6	−10
4	+19	+21	+29	+34	+36	+34	+30	+25	+19	+15	+11	+8	+6	+4	+2	+1	−1	−3	−6	−9	−13
2	+20	+21	+29	+34	+36	+34	+29	+24	+19	+14	+10	+7	+4	+2	+1	−1	−3	−6	−9	−13	−17
0	+20	+22	+30	+35	+37	+35	+31	+26	+20	+16	+11	+8	+5	+3	+1	−1	−4	−7	−11	−15	−19
−2	+21	+24	+33	+39	+41	+39	+36	+31	+26	+21	+17	+14	+11	+9	+7	+5	+2	−2	−6	−10	−15

Salinity, ppt

Table 5—continued

Temperature, °C	1000 dbar						2000 dbar						5000 dbar					
Salinity, ppt →	30	32	34	36	38	40	30	32	34	36	38	40	30	32	34	36	38	40
36																		
34																		
32	−2	−3	−4	−5	−6	−7	−2	−2	−3	−4	−5	−5	−3	−4	−4	−5	−6	−7
30	+7	+6	+6	+4	+3	+2	+8	+7	+7	+6	+5	+4	+8	+7	+6	+4	+3	+1
28	+11	+10	+9	+8	+6	+5	+13	+12	+11	+9	+8	+6	+14	+12	+10	+8	+5	+2
26	+12	+11	+10	+8	+6	+4	+14	+13	+11	+9	+7	+5	+17	+14	+11	+8	+4	+0
24	+11	+10	+8	+6	+4	+1	+13	+12	+10	+8	+5	+2	+17	+14	+10	+6	+1	−4
22	+10	+8	+6	+4	+1	−2	+12	+10	+8	+5	+2	−1	+17	+13	+9	+4	−2	−8
20	+9	+7	+5	+2	−1	−4	+11	+9	+6	+3	+0	−4	+17	+12	+7	+2	−5	−12
18	+8	+6	+4	+1	−2	−6	+10	+8	+6	+2	−1	−5	+17	+12	+7	+0	−6	−14
16	+8	+6	+4	+1	−2	−6	+10	+8	+5	+2	−2	−6	+17	+12	+7	+0	−7	−15
14	+8	+6	+4	+2	−1	−5	+11	+8	+6	+3	−1	−5	+18	+13	+7	+1	−7	−15
12	+8	+7	+5	+3	+0	−4	+11	+9	+7	+4	+0	−4	+19	+14	+8	+1	−6	−14
10	+8	+7	+5	+3	+0	−3	+11	+9	+7	+4	+0	−4	+18	+14	+8	+2	−6	−14
8	+8	+6	+5	+2	+0	−3	+10	+8	+6	+3	+0	−4	+17	+13	+7	+1	−6	−15
6	+6	+4	+3	+1	−2	−5	+7	+6	+4	+1	−2	−6	+15	+10	+5	−1	−9	−17
4	+3	+2	+0	−3	−5	−9	+4	+2	+0	−2	−6	−10	+11	+7	+2	−5	−12	−20
2	+0	−1	−3	−6	−9	−13	+1	−1	−3	−6	−10	−14	+7	+3	−2	−8	−16	−24
0	−1	−3	−5	−7	−11	−15	−1	−3	−5	−8	−12	−16	+5	+1	−4	−10	−17	−25
−2	+4	+2	+0	−3	−6	−10	+2	+1	−1	−4	−7	−11	+8	+4	+0	−5	−12	−19
−4																		

Salinity, ppt

Salinity, ppt	16 °C	20 °C	24 °C
42	−11	−11	−10
40	−8	−8	−7
38	−4	−4	−4
36	−1	−1	−1
34	+1	+1	+1
32	+3	+3	+3
30	+5	+5	+5
28	+7	+7	+7
26	+9	+9	+9
24	+11	+12	+12
22	+14	+15	+15
20	+18	+20	+20
18	+23	+24	+25
16	+29	+30	+30
14	+34	+35	+36
12	+38	+39	+40
10	+40	+41	+42
8	+38	+39	+40
6	+32	+33	+34
4	+23	+24	+25
2	+20	+20	+21

°C

ΔG_s

See footnote to Table 3.

Table 6. Values for ΔF (‰ × 10^3), the salinity difference between the PSS 78 and Ribe *and* Howe (1975) *calculated from the same measured values at pressures of 0, 1000, 2000, and 5000 dbar*

Pressure, 0 dbar

Temperature, °C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
36																						
34					+88	+49	+22	+5	−5	−11	−14	−15	−14	−13	−11	−10	−9	−8	−7	−8	−9	−10
32					+98	+58	+32	+15	+4	−2	−6	−7	−7	−6	−5	−4	−3	−3	−3	−4	−5	−7
30						+66	+40	+22	+11	+4	+1	−1	−1	−1	+0	+0	+1	+0	+0	−2	−4	−6
28						+74	+46	+28	+17	+10	+6	+4	+3	+3	+3	+3	+3	+2	+1	−1	−3	−6
26						+80	+52	+33	+21	+14	+9	+7	+5	+5	+4	+4	+3	+2	+1	−1	−4	−7
24						+85	+57	+38	+25	+17	+12	+9	+7	+6	+5	+4	+3	+2	+0	−2	−5	−8
22						+90	+61	+41	+28	+19	+14	+10	+8	+6	+5	+4	+3	+1	−1	−3	−6	−9
20						+94	+64	+44	+30	+21	+15	+11	+8	+7	+5	+4	+2	+1	−1	−4	−7	−10
18						+97	+67	+46	+32	+22	+16	+12	+9	+7	+5	+4	+2	+0	−2	−5	−7	−11
16						+99	+68	+47	+33	+23	+16	+12	+9	+7	+5	+4	+2	+0	−2	−5	−7	−10
14						+99	+69	+48	+33	+24	+17	+12	+9	+7	+5	+4	+2	+0	−2	−4	−7	−9
12						+98	+68	+47	+33	+23	+17	+13	+10	+8	+6	+5	+3	+1	−1	−3	−5	−8
10						+95	+66	+45	+32	+22	+16	+13	+10	+8	+7	+6	+4	+3	+1	−1	−4	−6
8						+88	+60	+41	+28	+20	+15	+12	+10	+8	+7	+6	+5	+4	+2	+0	−2	−5
6						+77	+51	+34	+23	+16	+12	+10	+9	+8	+8	+7	+6	+5	+3	+1	−1	−4
4					+96	+60	+37	+22	+13	+9	+6	+6	+6	+6	+6	+6	+6	+5	+3	+1	−2	−6
2					+67	+36	+16	+5	−1	−3	−3	−2	+0	+2	+3	+4	+3	+2	+0	−3	−6	−11
0				+70	+27	+1	−14	−20	−22	−21	−17	−14	−10	−6	−4	−3	−3	−4	−6	−10	−15	−21
−2			+69	+7	−29	−48	−55	−56	−52	−46	−39	−32	−26	−20	−17	−14	−14	−16	−19	−24	−31	−39
−4																						

Salinity, ppt

Table 6—continued

Temperature, °C	1000 dbar						2000 dbar						5000 dbar					
	30	32	34	36	38	40	30	32	34	36	38	40	30	32	34	36	38	40
36																		
34																		
32	+0	+1	+1	+1	+0	−2	+4	+5	+5	+5	+3	+1	+14	+15	+15	+14	+12	+10
30	+4	+4	+4	+3	+1	−1	+7	+8	+7	+6	+4	+1	+16	+17	+16	+15	+12	+8
28	+6	+6	+5	+3	+1	−2	+9	+9	+8	+6	+4	+0	+17	+17	+16	+14	+10	+6
26	+7	+6	+5	+3	+0	−3	+10	+9	+7	+5	+2	−1	+17	+16	+15	+12	+8	+3
24	+7	+5	+4	+2	−1	−5	+9	+8	+6	+4	+0	−4	+16	+15	+13	+10	+5	+0
22	+6	+5	+3	+0	−3	−7	+9	+7	+5	+2	−2	−6	+15	+14	+11	+7	+2	−4
20	+5	+4	+2	−1	−4	−8	+8	+6	+3	+0	−4	−8	+14	+12	+9	+5	+0	−7
18	+5	+3	+1	−2	−6	−9	+7	+5	+2	−1	−5	−10	+13	+11	+7	+3	−3	−9
16	+4	+2	+0	−3	−6	−10	+6	+4	+1	−2	−6	−11	+12	+10	+6	+2	−4	−11
14	+4	+2	+0	−3	−6	−10	+6	+4	+1	−2	−7	−11	+12	+10	+6	+1	−5	−12
12	+5	+3	+0	−2	−6	−10	+7	+4	+1	−2	−6	−11	+13	+10	+6	+1	−5	−12
10	+6	+4	+1	−1	−5	−9	+7	+5	+2	−2	−6	−11	+14	+11	+7	+2	−4	−12
8	+6	+5	+2	−1	−4	−8	+8	+6	+3	−1	−5	−11	+15	+13	+9	+4	−3	−11
6	+6	+5	+3	+0	−4	−8	+8	+6	+3	+0	−5	−11	+16	+14	+10	+5	−3	−11
4	+6	+4	+2	−1	−5	−10	+7	+6	+3	−1	−7	−13	+16	+14	+10	+5	−3	−13
2	+3	+2	−1	−4	−9	−15	+4	+3	+0	−5	−11	−18	+15	+13	+9	+3	−6	−17
0	−4	−5	−7	−11	−17	−24	−2	−3	−7	−12	−19	−28	+10	+9	+4	−3	−13	−26
−2	−16	−17	−19	−24	−32	−41	−14	−15	−19	−25	−34	−45	+1	+0	−5	−14	−26	−41
−4																		

Salinity, ppt

Salinity, ppt	16	20	24
42	−9	−10	−10
40	−6	−6	−6
38	−3	−4	−3
36	−1	−1	−1
34	+1	+1	+1
32	+3	+3	+2
30	+4	+4	+3
28	+6	+6	+4
26	+8	+7	+5
24	+10	+9	+6
22	+13	+11	+8
20	+17	+15	+11
18	+24	+21	+16
16	+33	+30	+24
14	+48	+44	+37
12	+69	+64	+56
10	+99	+94	+85
8			
6			
4			
2			

°C

ΔG_{B}

See footnote to Table 3.

Table 7. Values for ΔF (‰ × 10^3), the salinity difference between the PSS 78 and Fedorov (1971) *calculated from the same measured values at pressures of* 0, 500, 1000, *and* 2000 *dbar*

Pressure, 0 dbar

Temperature, °C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
36																						
34		+28	+38	+53	+64	+69	+70	+69	+67	+65	+64	+64	+65	+68	+72	+77	+81	+86	+90	+94	+97	+99
32		+26	+34	+48	+57	+61	+61	+58	+55	+51	+49	+47	+47	+48	+50	+53	+56	+59	+61	+63	+64	+64
30		+24	+31	+43	+51	+53	+52	+49	+44	+40	+36	+34	+32	+32	+33	+34	+36	+37	+38	+38	+37	+35
28		+22	+28	+39	+46	+47	+46	+41	+36	+31	+26	+23	+21	+20	+19	+20	+20	+20	+20	+18	+16	+13
26		+21	+26	+36	+42	+43	+41	+36	+30	+24	+19	+15	+12	+11	+10	+9	+8	+7	+5	+4	+1	−3
24		+20	+24	+33	+39	+40	+37	+32	+26	+20	+15	+10	+7	+5	+3	+2	+1	−1	−3	−6	−9	−14
22		+20	+23	+32	+37	+38	+35	+30	+24	+18	+12	+8	+4	+2	+0	−2	−3	−5	−8	−11	−15	−19
20		+20	+23	+31	+36	+37	+34	+29	+24	+18	+12	+8	+4	+1	−1	−3	−4	−6	−9	−12	−16	−21
18		+20	+22	+31	+36	+37	+35	+30	+25	+19	+14	+9	+6	+3	+1	−1	−3	−5	−7	−11	−14	−19
16		+20	+23	+31	+37	+38	+36	+32	+27	+21	+16	+12	+9	+6	+4	+3	+1	−1	−4	−7	−10	−14
14		+20	+23	+32	+38	+40	+38	+35	+30	+25	+20	+16	+13	+11	+9	+7	+6	+4	+1	−2	−5	−8
12		+21	+24	+34	+40	+42	+41	+38	+33	+28	+24	+20	+18	+15	+13	+12	+10	+8	+6	+4	+1	−2
10		+21	+25	+35	+42	+44	+44	+41	+37	+32	+28	+24	+21	+19	+17	+16	+14	+12	+10	+7	+5	+2
8		+22	+26	+36	+43	+46	+46	+43	+39	+35	+31	+27	+24	+21	+19	+17	+15	+12	+10	+7	+5	+3
6		+23	+27	+37	+45	+48	+47	+44	+40	+36	+31	+27	+23	+20	+17	+14	+11	+8	+5	+2	−1	−4
4		+23	+28	+38	+45	+48	+47	+44	+39	+34	+28	+23	+18	+14	+10	+5	+1	−3	−8	−12	−16	−19
2		+24	+28	+37	+44	+46	+44	+40	+34	+27	+20	+14	+7	+1	−6	−12	−18	−25	−31	−38	−44	−48
0		+24	+27	+35	+40	+41	+38	+32	+24	+15	+6	−4	−13	−22	−31	−41	−50	−60	−70	−79	−88	−95
−2		+23	+24	+31	+34	+32	+26	+18	+7	−5	−18	−31	−44	−57	−71	−85	−99					
−4																						

Salinity, ppt

Table 7—continued

Temperature, °C	500 dbar						1000 dbar						2000 dbar					
Salinity, ppt	30	32	34	36	38	40	30	32	34	36	38	40	30	32	34	36	38	40
36																		
34																		
32	+52	+56	+60	+63	+66	+68	+53	+58	+63	+67	+72	+75	+66	+73	+81	+89	+96	
30	+31	+34	+36	+38	+39	+39	+30	+34	+37	+40	+42	+44	+40	+46	+52	+58	+64	+69
28	+15	+16	+17	+18	+17	+16	+13	+15	+17	+19	+20	+20	+21	+25	+30	+35	+39	+43
26	+3	+3	+3	+3	+2	+0	+0	+1	+2	+3	+3	+3	+6	+10	+14	+18	+22	+25
24	−5	−6	−6	−7	−9	−11	−9	−9	−8	−8	−8	−9	−4	+0	+3	+7	+10	+13
22	−10	−11	−12	−13	−15	−17	−14	−14	−14	−14	−14	−15	−9	−6	−2	+1	+4	+7
20	−12	−12	−13	−15	−17	−19	−16	−16	−16	−16	−16	−17	−11	−8	−4	+0	+4	+7
18	−11	−11	−12	−14	−16	−18	−16	−15	−15	−14	−14	−15	−10	−6	−2	+2	+7	+11
16	−8	−9	−9	−10	−12	−14	−13	−12	−11	−11	−10	−10	−7	−2	+2	+7	+12	+18
14	−4	−5	−5	−6	−7	−8	−9	−8	−7	−6	−5	−4	−2	+2	+8	+14	+20	+26
12	+0	−1	−1	−2	−2	−3	−6	−4	−3	−2	+0	+2	+2	+7	+13	+20	+27	+34
10	+2	+2	+1	+1	+0	+0	−3	−2	+0	+1	+3	+5	+5	+11	+17	+25	+32	+41
8	+2	+2	+1	+0	+0	−1	−4	−3	−1	+1	+3	+5	+4	+11	+18	+25	+34	+43
6	−2	−4	−5	−6	−7	−8	−9	−9	−7	−6	−4	−2	−1	+5	+12	+20	+28	+38
4	−13	−16	−18	−21	−23	−24	−21	−22	−22	−21	−21	−19	−14	−9	−3	+4	+13	+22
2	−33	−38	−43	−47	−51	−54	−43	−45	−47	−49	−50	−49	−37	−34	−29	−24	−17	−8
0	−66	−74	−82	−89	−96		−78	−83	−88	−93	−96	−99	−75	−74	−72	−69	−64	−58
−2																		
−4																		

Salinity, ppt	16 °C	20 °C	24 °C
42	−11	−11	−12
40	−7	−8	−7
38	−4	−4	−4
36	−1	−1	−1
34	+1	+1	+1
32	+3	+3	+2
30	+5	+4	+3
28	+6	+5	+4
26	+8	+7	+6
24	+10	+9	+8
22	+14	+12	+12
20	+18	+16	+16
18	+22	+21	+21
16	+28	+27	+27
14	+33	+32	+33
12	+37	+37	+38
10	+39	+39	+40
8	+37	+38	+39
6	+32	+32	+34
4	+23	+23	+25
2	+20	+20	+21

Salinity, ppt

°C

ΔG_s

See footnote to Table 3.

Table 8. Conversion of sample profile from Ribe *and* Howe *(1975) to PSS 1978*

Pressure (dbar)	T_{68} °C	Salinity (‰)	ΔF‰ × 10^3	(S'−S)‰ × 10^3 ΔK Method	(S'−S)‰ × 10^3 ΔS Method
0	10.470	32.610	4.2	3.7	3.7
20	9.810	32.620	4.6	4.1	4.1
30	8.480	32.650	5.6	5.1	5.1
50	6.480	32.700	6.4	5.9	5.9
75	5.300	32.740	6.5	6.0	6.0
100	4.730	32.790	6.5	6.0	6.0
500	3.590	34.120	3.1	2.6	2.6
1000	2.850	34.390	1.1	0.6	0.6
2000	1.960	34.590	−0.5	−1.0	−1.0
4000	1.520	34.680	−1.2	−1.7	−1.7

The bottle sample was collected at 1000 m and analysed at 16°C to give the 34.39‰ value. From Table 6 (Ribe and Howe) $\Delta G_B = 0.6$, ΔF_B (1000 dbar) = 1.1 to give $(1 - K'/K) = 1.3 \times 10^{-5}$ (refer to equation 9).

In this case, the ΔK and ΔS methods differ by 0.003 salinity. Now using (9), (10) can be rewritten; $S' - S = \Delta F - (1 - K'/K)(a S_B + b S_B^2)$ and comparison with (8) shows that it is the difference between S and S_B that has allowed the results of the two methods to be different. It is also clear that if bS^2 is neglected with respect to aS that a ΔS correction proportional to S would be better than the commonly used simple additive constant.

Table 8 shows the conversion from Ribe and Howe (1975) of a sample profile taken at Ocean Station P in the North Pacific, 50°N, 145°W (July means). In this case the small range of salinity values results in identical ΔK and ΔS corrections.

RECOMMENDATIONS FOR DATA CONVERSION

From the above tables and examples it can be seen that much previously archived data in the oceanic range of salinities (33 to 37‰) will be within ±0.01‰ of salinity computed by the PSS 78 from the same measurements. Lewis and Perkin (1978) have estimated that ±0.01 is near the limit of accuracy achievable by the present CTD machines but the resulting profile is often calibrated to closer limits by single or multiple bottle sample analyses. Alternatively, many deep-sea oceanographers have used historical values as fixed points through which their measured profiles must pass. A typical salinity profile with an accuracy in salinity of ±0.01, precision ±0.003, and resolution of ±0.002 is 'pegged' by assuming the historical value at, say, 4000 m, is 'correct'. This means that the archived data will be assumed to be 'accurate' to within 0.002. Over the years the relationship between salinity and potential temperature for abyssal waters has been the same within experimental error [e.g., Reed (1969) for the Pacific]. If this is true at the measurement site then an *in situ* instrument can be calibrated accurately, at depth, simply by measuring the temperature and pressure and referring to the historical relationship for salinity. The continuing analysis of bottle samples serves to show any trend in the historical values.

Montgomery (1958) gave the characteristics of world oceanic water and showed that 99% of the water lies within a salinity range of 33 to 37. The change in salinity on conversion to the new scale for this salinity range can be found by reference to Table 2 and, over the normal range of laboratory temperatures used for bottle sample analysis, the change is very small. Therefore, for practical purposes, historical values will be preserved under the new scale. This is not necessarily the case for historical salinities derived from chlorinity because, as noted by Cox *et al.* (1967) the chlorinity-conductivity relationship varies as a function of depth and geographic location.

The use of historical values for calibration, although convenient, cannot be recommended over the procedure of bottle sample collection and analysis. There is some evidence that in addition to trends, unexpected temperatures (WONG, 1972) and salinities (FOFONOFF and TABATA, 1966) may occasionally appear even at great depth. Thus historical values, although providing a useful check, are no substitute for bottle samples in CTD calibrations.

If a decision should be made to convert large data files to their PSS 78 values, two approaches are recommended. The first and most direct is to gain access to the raw data and re-compute everything using PSS 78. If this can be accomplished without too much labour, it is the most desirable because it involves no approximation. The second recommended method is to enter the pertinent parts of the tables published in this paper and to interpolate the values of ΔG and ΔF needed for the ΔK or ΔS methods described above. Second-degree interpolation is recommended for rapidly changing parts of the tables. The advantage of the second method is that knowledge of the raw conductivity data is not necessary because the old salinity can be used to look up tabulated values. Bottle samples analysed on a bench salinometer can be corrected by the columns on the lower right of the various tables (ΔG_B) or by Table 2 if the International Tables were used to compute salinity. Note that the differences listed on Table 2 are almost independent of the temperature at which the bottle samples were analysed so that, for many cases, the correction could be made adequately from knowledge of the salinity alone. If enough bottle samples were used to correct the original profile, then conversion to PSS 78 could be accomplished merely by adjusting the original profile over by the amount by which the bottles had been changed. Obviously, each case would have to be examined to determine the errors involved in the simplification.

Variations in the chlorinity–conductivity relationship make it impossible to do a true conversion from chlorinity values into the PSS 78. Nevertheless, on occasions it may be necessary to attempt comparisons between data collected by the two techniques. The problem is best tackled by using the old relationship between chlorinity and salinity ($S = 1.80655\ Cl$) to obtain a salinity and then using the International Tables (UNESCO, 1966) which are based on 'average' seawater, to obtain a value of R_{15}. This value can then be used as K_{15} in equation (1) of the Appendix to obtain a practical salinity. Alternately, the R_{15} value can be used in new oceanographic tables of practical salinity as a function of conductivity ratio, to be published by UNESCO shortly. It must be emphasized that the conversion procedure is improper in terms of the definition of the PSS 78 and is offered here only as a best solution. Practical salinities so derived have uncertain errors though normally they are unlikely to exceed ± 0.03. Although uncertainties due to variations in ionic content remain it is worth noting that salinities computed from chlorinity by the Knudsen equation ($S = 0.03 + 1.805\ Cl$) are in much better agreement with the new scale. Differences are reduced to within ± 0.001 over the range $25 < S < 38$ provided the water studied has a composition that can be described properly by the original chlorinity–conductivity relationship of Cox *et al.* (1967) on which the International Tables are based.

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APPENDIX

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 is defined for reporting oceanographic observations.

(2) The practical salinity, symbol S, of a sample of seawater, is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15°C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32.4356×10^{-3}, at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds, by definition, to a practical salinity exactly equal to 35. The practical salinity is defined in terms of the ratio K_{15} by the following equation:

$$S = a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} + a_4 K_{15}^2 + a_5 K_{15}^{5/2}, \tag{1}$$

$$\begin{aligned} a_0 &= 0.0080 \\ a_1 &= -0.1692 \\ a_2 &= 25.3851 \\ a_3 &= 14.0941 \\ a_4 &= -7.0261 \\ a_5 &= 2.7081 \\ \sum a_i &= 35.0000 \\ 2 \leqslant S &\leqslant 42. \end{aligned}$$

As a consequence of this definition any oceanic water having a precisely known conductivity ratio of near unity at 15°C with the KCl solution is a secondary standard for routine calibration of oceanographic instruments. All seawaters having the same conductivity ratio have the same practical salinity. Chlorinity is to be regarded as a separate, independent variable in describing the properties of seawater. It should be noted that the Practical Salinity values are 1000 times the values of the salinity of the same samples of seawater obtained on the previous scales. For instance, a sample of seawater having a salinity of 0.03512 (i.e., 35.12‰) will have a practical salinity of 35.12.

Algorithm for in situ *data*

Given *in situ* measurements of conductivity ratio

$$R = \frac{C(S, T_{68}, p)}{C(35, 15_{68}, p)},$$

temperature T_{68} °C, and pressure p dbar, R_T can be computed as follows:

$$R_T = \frac{R}{r_T R_p}.$$

$$R_p = (1 + \alpha),$$

where

$$\alpha = \frac{A_1 p + A_2 p^2 + A_3 p^3}{1 + B_1 T + B_2 T^2 + B_3 R + B_4 T R} \tag{2}$$

and

$$\begin{aligned} A_1 &= 2.070 \times 10^{-5} \\ A_2 &= -6.370 \times 10^{-10} \\ A_3 &= 3.989 \times 10^{-15} \\ B_1 &= 3.426 \times 10^{-2} \\ B_2 &= 4.464 \times 10^{-4} \\ B_3 &= 4.215 \times 10^{-1} \\ B_4 &= -3.107 \times 10^{-3} \end{aligned}$$

$$r_T = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4 \tag{3}$$

$$\begin{aligned} c_0 &= 6.766097 \times 10^{-1} \\ c_1 &= 2.00564 \times 10^{-2} \\ c_2 &= 1.104259 \times 10^{-4} \\ c_3 &= -6.9698 \times 10^{-7} \\ c_4 &= 1.0031 \times 10^{-9}. \end{aligned}$$

Note that the value for c_3 was given incorrectly as −6.9689 in LEWIS (1980).

Salinity can be calculated from R_T and T by the following polynomials:

$$S = a_0 + a_1 R_T^{1/2} + a_2 R_T + a_3 R_T^{3/2} + a_4 R_T^2 + a_5 R_T^{5/2} + \frac{(T-15)}{1+k(T-15)}\{b_0 + b_1 R_T^{1/2} + b_2 R_T + b_3 R_T^{3/2} + b_4 R_T^2 + b_5 R_T^{5/2}\}, \qquad (4)$$

where the values of a_i have been given below equation (1) in this appendix and

$b_0 = 0.0005$ $k = 0.0162$
$b_1 = -0.0056$
$b_2 = -0.0066$
$b_3 = -0.0375$
$b_4 = 0.0636$
$b_5 = -0.0144$

$\sum b_i = 0.0000.$

Ranges of validity

$$2 \leqslant S \leqslant 42$$
$$-2°C \leqslant T \leqslant 35°C$$
$0 \leqslant p \leqslant 10{,}000$ dbar for all deep ocean waters.

For bench salinometer use, the last equation can be used alone, though it is to be noted that R_T is then a measured value, R_T.

CONCLUSION

DEFINITION AND ALGORITHM OF PRACTICAL SALINITY

During its last meeting in September 1980, the Joint Panel on Oceanographic Tables and Standards drafted a document on the Practical Salinity Scale and the International Equation of State for Seawater. In conclusion, and set out hereunder, is a reproduction of the section of this document relative to the definition of the Practical Salinity Scale and to the algorithm for the calculation of practical salinity from in situ conductivity measurements. The following equations are to be used to compute practical salinity.

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 is defined for reporting oceanographic observations.

2. The practical salinity, symbol S, of a sample of seawater, is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15°C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32.4356×10^{-3}, at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds, by definition, to a practical salinity exactly equal to 35. The practical salinity is defined in terms of the ratio K_{15} by the following equation :

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

$a_0 = 0.0080$
$a_1 = -0.1692$
$a_2 = 25.3851$
$a_3 = 14.0941$
$a_4 = -7.0261$
$a_5 = 2.7081$
$\Sigma a_i = 35.0000$
$2 \leqslant S \leqslant 42$

As a consequence of this definition, any oceanic water having a precisely known conductivity ratio of near unity at 15°C with the KCl solution is a secondary standard for routine calibration of oceanographic instruments. All seawaters having the same conductivity ratio have the same practical salinity. Chlorinity is to be regarded as a separate, independent variable in describing the properties of seawater.

It should be noted that the practical salinity values are 1000 times the values of the salinity of the same samples of seawater obtained on the previous scales. For instance, a sample of seawater having a salinity of 0.035 12 (i.e., 35.12 °/oo) will have a practical salinity of 35.12.

The Algorithm for Practical Salinity

If R_t is the ratio of the conductivity of seawater, at temperature t, to the conductivity of seawater of practical salinity 35 at the same temperature (both at a pressure of 1 standard atmosphere), then R_{15} will have the same value as K_{15}, and may, therefore, be used to calculate practical salinity in equation 1. Since all practical salinity measurements are carried out in reference to the conductivity of standard seawater (corrected to $S = 35$), it is the quantity R_t which will be available for salinity calculations. R_t is normally obtained directly by laboratory salinometers, but in situ measurements usually produce the quantity R, the ratio of the in situ conductivity to the standard conductivity at $S = 35$, $t = 15^{\circ}C$, $p = 0$ (where p is the pressure above one standard atmosphere). R is factored into three parts, i.e.,

$$R = R_p r_t R_t \tag{2}$$

R_p is the ratio of the in situ conductivity to the conductivity of the same sample at the same temperature but at $p = 0$; r_t is the ratio of the conductivity of reference seawater, having a practical salinity of 35, at temperature t, to its conductivity at $t = 15^{\circ}C$. A knowledge of R_p and r_t allows the calculation of R_t from the in situ results, i.e.,

$$R_t = \frac{R}{R_p r_t} \tag{3}$$

It has been found that R_p, r_t and R_t can be expressed as functions of the numerical values of the in situ parameters, R, t and p, when t is expressed in °C and p in bars (10^5Pa), as follows

$$R_p = 1 + \frac{p(e_1 + e_2 p + e_3 p^2)}{1 + d_1 t + d_2 t^2 + (d_3 + d_4 t)R} \tag{4}$$

where

$e_1 = 2.070 \times 10^{-4}$
$e_2 = -6.370 \times 10^{-8}$
$e_3 = 3.989 \times 10^{-12}$

$d_1 = 3.426 \times 10^{-2}$
$d_2 = 4.464 \times 10^{-4}$
$d_3 = 4.215 \times 10^{-1}$
$d_4 = -3.107 \times 10^{-3}$

and

$$r_t = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + c_4 t^4 \tag{5}$$

where

$$c_0 = 0.676\,609\,7$$
$$c_1 = 2.005\,64 \times 10^{-2}$$
$$c_2 = 1.104\,259 \times 10^{-4}$$
$$c_3 = -6.9698 \times 10^{-7}$$
$$c_4 = 1.0031 \times 10^{-9}$$

The effect of the relatively small differences between R_t and R_{15} at a given salinity can be accounted for by adding a correction, ΔS, to the practical salinity calculated by substitution of R_t for K_{15} in equation 1. The practical salinity, therefore, may be computed with the equation

$$S = a_0 + a_1R_t^{1/2} + a_2R_t + a_3R_t^{3/2} + a_4R_t^2 + a_5R_t^{5/2} + \Delta S \qquad (6)$$

where

$$\Delta S = \frac{(t-15)}{1 + k(t-15)} \left(b_0 + b_1R_t^{1/2} + b_2R_t + b_3R_t^{3/2} + b_4R_t^2 + b_5R_t^{5/2}\right)$$

with the constants a_i defined in equation 1 and

$$b_0 = 0.0005$$
$$b_1 = -0.0056$$
$$b_2 = -0.0066 \qquad k = 0.0162$$
$$b_3 = -0.0375$$
$$b_4 = 0.0636$$
$$b_5 = -0.0144$$
$$\Sigma b_i = 0.0000$$

The equations 4, 5 and 6 are valid over the ranges of temperature (-2 to 35°C), pressure (0 to 1000 bars), and practical salinity (2 - 42) in the world ocean.

For laboratory salinometers the calculation of practical salinity requires only equation 6. For calculations based on in situ measurements, one must compute R_p and r_t from equations 4 and 5 respectively, and then compute R_t from equation 3. Practical salinity can then be computed from equation 6.

The following values are provided for checking the correct use of the above equations.

R	$t(^{\circ}C)$	p(bars)	R_p	r_t	R_t	S
1	15	0	1.000 000 0	1.000 000 0	1.000 000 0	35.000 000
1.2	20	200	1.016 942 9	1.116 492 7	1.056 887 5	37.245 628
0.65	5	150	1.020 486 4	0.779 565 85	0.817 058 85	27.995 347

Additional Remarks

Limitation of the equations

The practical salinity scale and the algorithm to calculate practical salinity are meant for use in all oceanic waters. However, these equations should be used with caution in waters that have a chemical composition different from standard seawater. Salinities determined by laboratory salinometers operated at widely different temperatures may differ measurably due to possible changes in the temperature dependence of conductivity ratio with changing composition of chemicals.

Conversion of existing data based on previous salinity scales

For comparison with new data, salinities based on previous scales must be converted to the practical salinity scale. The conversion procedures are presented in Unesco Technical Papers in Marine Science No. 37 (Unesco, 1981,b).

Practical Salinity Standards

Because salinometers calibrated at a single point often have linear offsets, a low salinity standard ($S =$ *ca* 30) will be made available by the Standard Seawater Service before the end of 1981. This standard (L series) must be used solely to check the offsets of salinometers, and not as a main standard. The P series standard ($S =$ *ca* 35) remains the one to use for calibration of salinometers.

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No.		Year	SCOR WG
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9	Report on intercalibration measurements, Leningrad, 24-28 May 1966 and Copenhagen, September 1966; organized by ICES	1969	-
10	Guide to the Indian Ocean Biological Centre (IOBC), Cochin (India), by the Unesco Curator 1967-1969 (Dr. J. Tranter)	1969	-
12	Check-List of the Fishes of the North-Eastern Atlantic and of the Mediterranean (report of the third meeting of the Committee, Hamburg, April 1969)	1969	-
13	Technical report of sea trials conducted by the working group on photosynthetic radiant energy, Gulf of California, May 1968; sponsored by SCOR, IAPSO, Unesco	1969	WG 15
14	Incorporated with Nos. 1, 4 and 8 in No. 27	1970	WG 10
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