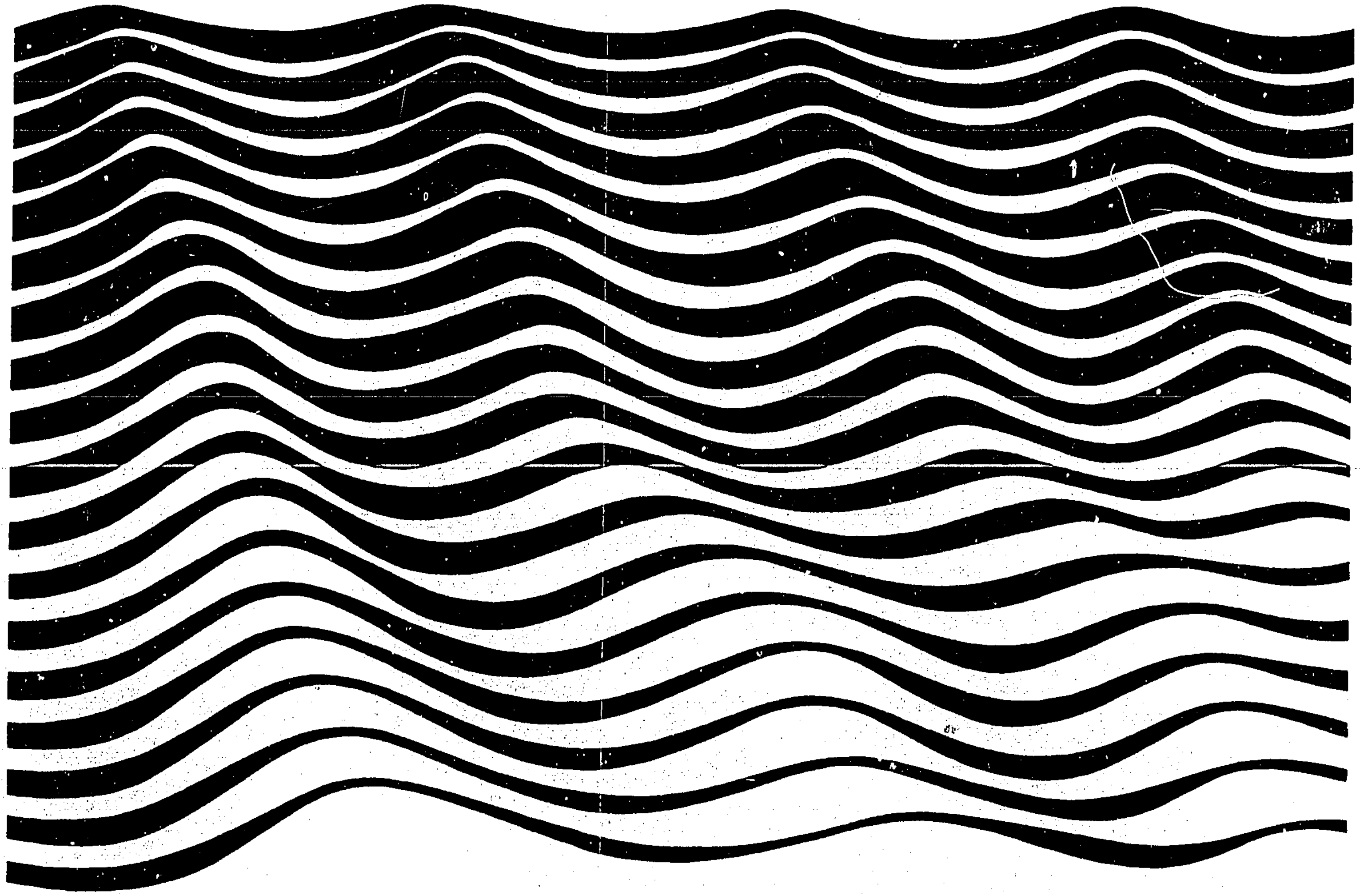
Unesco technical papers
in marine science 24

Seventh report of the joint panel on oceanographic tables and standards

Grenoble, France
2-5 September 1975
sponsored by
Unesco, ICES, SCOR, IAPSO



Unesco 1976

UNESCO TECHNICAL PAPERS IN MARINE SCIENCE

Numbers 1 to 8, 10 to 12, 14 are out of stock. For full titles see inside back cover

No.		Year	SCOR WG
9	Report on intercalibration measurements, Leningrad, 24-28 May 1966 and Copenhagen, September 1966; organized by ICES	1969	–
11	An intercomparison of some current meters, report on an experiment at WHOI Mooring Site "D", 16-24 July 1967 by the working group on Continuous Current Velocity Measurements. Sponsored by SCOR, IAPSO and Unesco	1969	WG 21
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
15	Monitoring life in the ocean; sponsored by SCOR, ACMRR, Unesco, IBP/PM	1973	WG 29
16	Sixth report of the joint panel on oceanographic tables and standards, Kiel, 24-26 January 1973; sponsored by Unesco, ICES, SCOR, IAPSO	1974	WG 10
17	An intercomparison of some current meters,report on an experiment of Research Vessel Akademic Kurchatov, March-April 1970, by the working group on Current Velocity Measurements; sponsored by SCOR, IAPSO, Unesco	1974	WG 21
18	A review of methods used for quantitative phytoplankton studies; sponsored by SCOR, Unesco	1974	WG 33
19	Marine Science Teaching at the University Level. Report of the Unesco Workshop on University Curricula – *Also published in French and Spanish*	1974	—
20	Ichthyoplankton. Report of the CICAR. Ichthyoplankton Workshop *Also published in Spanish*	1975	–
21	An intercomparison of open sea tidal pressure sensors. Report of SCOR Working Group 27: "Tides of the open sea"	1975	WG 27
22	European sub-regional co-operation in oceanography. Report of a working group sponsored by the Unesco Scientific Co-operation Bureau for Europe and the Division of Marine Sciences	1975	—
23	An intercomparison of some current meters, III. Report on an experiment carried out from the Research Vessel Atlantis II, August-September, 1972, by the Working Group on Continuous Velocity Measurements: sponsored by SCOR, IAPSO and Unesco	1975	WG 21

Unesco technical papers
in marine science 24

Seventh report of the joint panel on oceanographic tables and standards

Grenoble, France
2-5 September 1975
sponsored by
Unesco, ICES, SCOR, IAPSO

Unesco 1976

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.

Unesco Technical Papers in Marine Science are distributed free of charge to various institutions and governmental authorities. Requests for copies of individual titles or additions to the mailing list should be addressed, on letterhead stationery if possible, to:

Division of Marine Sciences
Unesco
Place de Fontenoy
75700-Paris, France

FOREWORD

Members of the Panel, as well as other interested scientists, may wish to refer to their past deliberations. The following meetings of the Joint Panel on Oceanographic Tables and Standards have taken place and reports published :

1. First Report, Copenhagen, 1964, Unesco Technical Papers in Marine Science 1;*
2. Second Report, Rome, 1965, Unesco Technical Papers in Marine Science 4;*
3. Third Report, Berne, 1967, Unesco Technical Papers in Marine Science 8;*
4. Fourth meeting, Fort Lauderdale, 1969, no report produced;
5. Fifth Report, Kiel, 1969, Unesco Technical Papers in Marine Science 14;*
6. Sixth Report, Kiel, 1973, Unesco Technical Papers in Marine Science 16.

The Joint Panel on Oceanographic Tables and Standards was preceded by the Joint Panel on the Equation of State of Sea Water, which was disbanded after having had two meetings. These meetings were held in Paris, 23-25 May 1962 and Berkeley, 16-18 August 1963. The reports of these meetings were not widely distributed, being issued only as internal Unesco reports (code NS/9/114B).

These two reports are attached as Appendices I and II to the Seventh Report of the Joint Panel, which constitutes the main body of this document. It would seem desirable to have the whole narrative of the Joint Panel available to the oceanographic community, in view of the proposed replacement of the Knudsen-Ekman equation of state of sea water.

---

* Unesco Technical Papers in Marine Science, N° 27 : "Collected Reports of the Joint Panel on Oceanographic Tables and Standards, 1964-1969" is a reprint of the first, second, third and fifth reports. A limited number of copies is available on request.

TABLE OF CONTENTS

I. INTRODUCTION

The Panel opened its session at 9.00 a.m., Tuesday 2 September 1975, in the University for Languages and Letters on the University Campus of Saint-Martin d'Hères, Grenoble, France.

At its sixth meeting (1973) in Kiel, it was decided to hold the seventh meeting of the Panel in conjunction with the XVI General Assembly of the International Union of Geodesy and Geophysics (IUGG) in September 1975 in Grenoble, following the recommendation of the Unesco representative on the Panel, thereby reducing travel expenses.

The organizer of the IUGG General Assembly scheduled the meeting for the Panel for three full days on 2, 4 and 5 September 1975.

The following members of the Panel attended the meeting :

Professor Dr. K. Grasshoff (Chairman)	Institut für Meereskunde, D-23 Kiel, F.R.G.	SCOR
Professor J. Gieskes	Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, USA	SCOR
Dr. N.P. Fofonoff	Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543, USA	IAPSO
Prof. Dr. W. Kroebel	Institut für Angewandte Physik, D-23 Kiel, F.R.G.	IAPSO
Dr. G.N. Ivanov-Franzkevich	Institute of Oceanology, 1 Letniaya Zh-387 Moscow 109387, USSR	Unesco
Dr. O. Mamayev	Intergovernmental Oceano- graphic Commission, Unesco, Place de Fontenoy, 75700 Paris, France	Unesco/IOC
Mr. M. Menaché	Institut Océanographique, 195, rue St. Jacques 75005 Paris, France	Unesco
Dr. F. Culkin	Institute of Oceanographic Sciences, Wormley, Godalming, Surrey, England	ICES

Mr. C.K. Ross	Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography Dartmouth, Nova Scotia, Canada	ICES
Dr. A. Poisson	Laboratoire d'Océanographie Physique, Université P. et M. Curie Tour 24, 4 Place Jussieu, 75230 Paris, Cedex 05, France	ICES
Prof. F. Millero	Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Florida 33149 USA	co-opted member (2 September only)

Dr. F. Fisher (Scripps Institution of Oceanography, University of California, San Diego) for SCOR was unable to attend and has since expressed his wish to resign from the Panel.

The following experts and/or representatives were also present during portions of the meeting :

Dr. D. Krause	Division of Marine Sciences, Unesco Place de Fontenoy, 75700 Paris, France	Unesco
Dr. S.A. Morcos	ibid.	Unesco
Dr. P. Brewer	Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543, USA	
Dr. E.L. Lewis	Frozen Sea Research Group Department of the Environment 825 Devonshire Road Victoria, British Columbia, Canada.	

The Chairman welcomed the members and introduced the two new members of the Panel, Mr. C. Ross and Dr. A. Poisson, both nominated by ICES and replacing Prof. O. Saelen and Mr. F. Hermann. He also introduced Prof. F. Millero, whom the Panel suggested as an additional member during its sixth meeting.[*]

---

[*] See Unesco Technical Papers in Marine Science 16, "Sixth Report of the Joint Panel on Oceanographic Tables and Standards".

The following agenda was adopted for the seventh meeting of the Panel :

1. Opening of the meeting.
2. Adoption of the agenda.
3. Review of the work done in the time since the sixth meeting of the Panel.
4. Report on the present knowledge on the transformation of in situ conductivity into salinity and density.
5. Report on the progress made in measuring the absolute conductivity of sea water (Culkin, Poisson).
6. Concluding remarks on the oxygen saturation value tables.
7. Matters related to the equation of state of sea water with a progress report by Gieskes and Millero.
8. Matters related to the determination of the absolute density of pure water and sea water.
9. Matters related to the entropy of sea water.
10. Suggestions (if any) on further oceanographic tables.
11. Election of the chairman for the next period.
12. Date and place of the next meeting.

Because Professor Millero was able to attend the meeting on 2 September 1975 only, items 7 and 9 were discussed during the first day of the meeting.

II. REPORT BY AGENDA ITEM

1. Review of work since sixth meeting (item 3)

The Panel was informed by Professor Kroebel that new precise and accurate measurements of sound velocity in pure water and sea water have been made at atmospheric pressure (Kroebel and Mahrt, 1975). Some considerable deviations between old measurements and the new ones were found. The Panel congratulated Professor Kroebel on his excellent work and shared the opinion that these recent determinations are likely to represent the most accurate absolute determinations of the sound velocity in sea water, and encouraged the speedy publication of this work. The Panel felt that, in the near future, the old tables of sound velocity as a function of salinity, temperature and pressure must be replaced on the basis of the new measurements. The Panel further felt that redeterminations of the sound velocity in pure water and sea water should be encouraged, especially in the light of the importance of reliable data for mapping the sea floor. The Panel urged Professor Kroebel to continue this work.

The Panel was also informed that new measurements had been made of the thermal expansion, the specific volume (Chen and Millero, 1975; Millero et al., 1975) and the freezing point of sea water (Fujino et al., 1974; Doherty and Kester, 1974). The sea water freezing point measurements, in particular, should receive due attention in the future work of the Panel.

2. Transformation of in situ conductivity into salinity and density (item 4)

The Panel was informed by the chairman that Dr. Fisher had been unable to prepare the report on the procedures for the conversion of the conductivity obtained by in situ instruments into other parameters, such as salinity. The Panel felt unable to take up this serious matter without a background paper, circulated in advance of the meeting. In spite of the importance of consolidating and unifying the conversion procedures, no generally adopted and recommended procedure is available.

Furthermore, the Panel noticed that no reaction has taken place with respect to the recommendation 1/1973 of the Panel (given at the end of this report). In the meantime, the reliability and precision of in situ conductivity instruments improved considerably, and the use of such instruments has greatly increased, making the adoption of a uniform conversion procedure still more important and urgent. Therefore, the Panel decided to reinforce Recommendation 1/1973 (see Annex I) and to ask SCOR and IAPSO to identify institutes which are prepared to determine temperature coefficients of the conductivity of sea water in the range not covered by the International Oceanographic Tables. The resultant Recommendation 2/1975 of the Joint Panel is attached to this report (Annex I).

The chairman reported on the performance and evaluation of a bench-type salinometer intercalibration exercise carried out under the auspices of the IAPSO Standard Seawater Service and ICES on the basis of low salinity Baltic sea water samples (≃ 8 ‰ S) and Mediterranean sea water samples (≃ 38‰ S). The result of this intercomparison was rather alarming in showing very clearly that the commercially available bench-type salinometers are not calibrated within the range of precision of these instruments. Deviations as large as 0.1 ‰ occurred at the lower salinities and 0.01 ‰ at the higher salinities. The results of this intercalibration exercise are attached to this report as Annex II. The Panel was of the opinion that the manufacturers of bench-type salinometers should be requested to provide certificates ensuring the consistancy of the calibration between instruments, for example on the basis of the low and high salinity standards provided by the Standard Seawater Service. Furthermore, the Panel **recommends** that the users of salinometers should frequently carry out a careful check of the internal calibration and the temperature compensation in the more extreme ranges of salinity by means of calibration against Standard Seawater samples.

3. Measurement of absolute electrical conductivity of sea water (item 5)

Dr. Culkin reported on this item. No measurements of the absolute electrical conductivity of Standard Seawater have yet been carried out at the Institute of Oceanographic Sciences, Wormley (formerly National Institute of Oceanography), but the work is intended to be carried out. Dr. Poisson reported on his comparison measurements of different batches of Standard Seawater relative to potassium chloride (Annex III). A maximum deviation of the conductivities equivalent to an apparent salinity deviation of up to 0.006 ‰ was obtained at 25°C. No simple explanation for these different conductivities for equal nominal chlorinities of the Standard Seawater could be given.

The Panel considered these findings as serious and recommended that at least two institutes (specifically Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada and Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Florida 33149, USA) should reconfirm the appearance of such deviations by comparing the relative conductivity of different batches of Standard Seawater with the most precise bench-type salinometer now available (Guildline Salinometer). The Standard Seawater Service will provide these two institutes with the necessary samples. Before taking any further decisions, the Panel would like to have the findings of Dr. Poisson carefully reconfirmed through the measurements mentioned above. The Panel will take up this problem at its next meeting and has asked Dr. Culkin and Dr. Poisson to consider the possible consequences and report to the Panel.

4. Oxygen saturation value tables (item 6)

The chairman reported on this item. Since the sixth meeting of the Panel, the second volume of the International Oceanographic Tables has been printed and is now available through the national distributors of Unesco publications. An announcement has been made in several oceanographic journals. It has already appeared in "Marine Chemistry" and "Okeanologiya" (in Russian) and is in press in "Deep Sea Research". The volume contains tables for the oxygen saturation of sea water and conversion tables for salinity/chlorosity.

5. Equation of state of sea water (item 7)

Prof. Gieskes and Prof. Millero gave a brief summary on the present state of development and referred especially to the symposia on "Physical Chemistry and Inorganic Chemistry of Sea Water" and "Thermodynamics of the Sea and Equation of State", organized during the concurrent IUGG General Assembly and chaired by Prof. Gieskes and Prof. Millero.

The Panel noted with concern that the new accurate and independent measurements of the specific volume of sea water and of the pressure and thermal coefficients show a systematic deviation from the generally accepted and currently used data of Knudsen and Ekman. The general opinion of the Panel was that undoubtedly these deviations make necessary the consideration of the replacement of the hitherto accepted equation of state by a new equation of state.

Such a replacement requires a crucial decision with obvious consequences in its implementation, but this improvement of the measurement of the thermodynamic properties of sea water cannot be disregarded by the oceanographic community. The most suitable form of a new equation of state seems to be a modification of the one proposed by Millero and co-workers in 1975.

A logical consequence of the introduction of a new equation of state would also be that all thermodynamic properties would be given for "sea water", that is, Standard Seawater evaporated or weight diluted with distilled water. This would make the term "salinity" consistent with the concept as required in the new equation of state. It appeared very clearly during the discussion that the "salinity", as defined through the equation for the relative conductivity, the Unesco Oceanographic Tables and the equation

$$S ‰ = 1.80655 \times Cl ‰ ,$$

is not in conformity with the term "salinity" as applied in the equation of state. For further application regarding sea water with anomalies in its composition (e.g., Baltic water, Black Sea water, Pacific deep water with high silicate content), a correction of the measured "salinity" must be used, possibly with a special correction term proportional to the measured "salinity" or chlorinity, before entering the "salinity" into the new equation of state.

It was decided that before taking any firm decisions and before recommending the general acceptance of a new equation of state, comments from the oceanographic community should be invited. For this purpose a note was drafted which summarizes the problem and gives all necessary references. This note is in the form of a "Letter to the Editor" and is to be widely distributed through most appropriate channels in order to make the oceanographic community aware of the situation. The note is attached to this report as Annex IV.

It was decided that the note should be signed by the chairman of the Panel in the name of the Panel and forwarded to the following journals:

Okeanologiya (U.S.S.R.)
Deep Sea Research
Journal of the Oceanographic Society Japan
Journal of Physical Oceanography.

Such a step should provide for a procedure in which the oceanographers concerned can submit arguments for and against the approval of a new equation of state which the Panel in due course can consider before a new equation of state will be recommended.

6. Determination of absolute density of pure water and sea water (item 8)

Mr. Menaché recalled the Resolution 1/1969 of the Joint Panel regarding the redetermination of the absolute density of water between 0 and 30 °C, a resolution which had been endorsed in 1970 by IAPSO and in 1971 by IUGG. He then informed the Panel that a similar recommendation was made in 1974 by the Commission I.4 (Physicochemical Measurements and Standards) of the International Union of Pure and Applied Chemistry (IUPAC), which has received a wide diffusion and has already been put into application. An informal document was prepared by Mr. Menaché and distributed to the Panel. An abbreviated version of this paper is attached as Annex V. Hopefully within a period between 5 and 10 years, new measurements of the absolute density of water will be arrived at and reliable results obtained.

In the meantime, IUPAC recommends the exclusive use of a proposed provisional table of the absolute density of Standard Mean Ocean Water (SMOW) between 0 and 40 °C. This table is computed from that of Bigg, by adopting for SMOW the provisional value of ρ_{max} (SMOW) equals 999.975 kg m^{-3}. A fifth order polynomial was used to calculate this table.

This would at least provide a uniform basis for future measurements until absolute densities are known and would facilitate transformation of later intermediate data.

A resolution (see Resolution 1/1975) **was** issued by the Panel endorsing those of IUPAC in favour of new determinations of the absolute density of water between 0 and 40°C. It recommends meanwhile the exclusive use of the table of the absolute density of **SMOW between 0 and 40 °C proposed by IUPAC, for the determination of absolute density of sea water with reference to pure water. This resolution was adopted by IAPSO during the IUGG General Assembly. A similar resolution was forwarded to IUGG for consideration and possible adoption.***

---

* This latter resolution was in turn adopted by the Session of the IUGG General Assembly on 6 September 1975, acting upon the resolutions of the Panel and **IAPSO** (see Annex VI)

The IUPAC table of the absolute density of SMOW between 0 and 40°C, with an explanatory text, is attached in annex V to this report.

7. Entropy of sea water (item 9)

The Panel briefly discussed problems related to the entropy of sea water, referring to the papers and discussion presented at the symposium of the "Thermodynamics of the Sea and Equation of State" of the IUGG General Assembly. It was decided to reconsider this matter after a decision had been made regarding the new equation of state.

8. Further oceanographic tables (item 10)

The Panel foresees that no new oceanographic tables will be proposed within the forthcoming intersessional period. However, if a new equation of state is adopted and recommended at the next meeting of the Panel, several new tables are likely to be recommended by the Panel. The volume and format of these new tables should correspond to the needs of the users by giving all details for computerisation of the calculations needed for the more precise treatment, and by not becoming bulky through being too comprehensive. It is likely that, commencing 1977, one table will be proposed for printing each year.

9. Next chairman (item 11)

Prof. Grasshoff was re-elected chairman for the coming period.

10. Date and place of next meeting (item 12)

The Panel suggested having its next meeting in May 1977 and asked Dr. Fofonoff to investigate whether this meeting could be held at the Woods Hole Oceanographic Institution (Woods Hole, Massachusetts, USA).* The main topic of the next meeting will be the matters related to the new equation of state, the conversion of the in situ conductivity, and the new measurements of the freezing point of sea water.

The Panel discussed its present membership and was strongly in favour of the inclusion of Dr. E.L. Lewis from the Department of the Environment, Canada, as an expert on the in situ conductivity problem. Dr. Lewis might serve as replacement for Dr. Fisher (SCOR). The chairman was asked to approach SCOR in this matter. The Panel was pleased that Dr. Lewis is willing to prepare a background paper on the present situation of the conversion of in situ conductivities into salinities which will be circulated to members of the Panel well in advance of the next meeting.

---

* In the meantime, an official invitation to hold the meeting in Woods Hole in the second half of May 1977 has been received.

The Panel discussed also the need for the invitation of experts on the physical chemistry of sea water to the next meeting to provide for the necessary competence when the new equations of state will be discussed and recommended. The Panel will discuss possible invitations by correspondence and approach Unesco and SCOR for support.

The meeting closed at noon on 5 September 1975.

K. Grasshoff
Chairman

III. REFERENCES

Chen, Chen-Tung; Millero, F.J. 1975. The specific volume of sea water at high pressures. Deep-Sea Res. (in press)

Doherty, B.T.; Kester, D.R. 1974. Freezing point of sea water. J. Mar. Res., Vol. 32, No. 2, p. 285-300.

Fujino, K.; Lewis, E.L.; Perkin, R.G. 1974. The freezing point of sea water at pressures up to 100 bars. J. Geophys. Res., Vol. 79, No. 12, p. 1792-7.

Kroebel, W.; Mahrt, K.H. 1975. Recent results of absolute sound velocity measurements in pure water and sea water at atmospheric pressure. Inst. of Appl. Physics, Kiel University, FRG, (unpublished manuscript)

Millero, F.J.; Gonzalez, A.; Ward, G.K. 1975. The density of sea water solutions at one atmosphere as a function of temperature and salinity. J. Mar. Res. (in press)

Recommendation 1/1973

Taking into account the rapidly increasing use of <u>in situ</u> measurements of conductivity for estimating salinity and considering that no internationally accepted conversion formulae have been recognized, the Panel strongly recommends that IAPSO, IUGG, SCOR, ICES and Unesco take steps so that :

a) Precise measurements of conductivity ratios of sea water be carried out in the range -2 to 15°C to extend the range of present Unesco tables to lower temperatures;

b) precise measurements of conductivity ratio of sea water be carried out at elevated pressures to verify and extend the salinity range of the present Bradshaw and Schleicher formula;

c) after suitable evaluation, the panel propose a conversion procedure for estimating salinity from <u>in situ</u> measurements of conductivity, temperature and pressure for international use;

d) a working group be formed to initiate and carry out intercalibration procedures for <u>in situ</u> measurements of conductivity, temperature and pressure.

Recommendation 1/1975

The UNESCO/ICES/SCOR/IAPSO Joint Panel of Experts on Oceanographic Tables and Standards :

- referring to the Recommendation 1/1969 of the Joint Panel in favour of new determinations of the absolute density of water and its thermal expansion in the range of 0 – 40°C, which Recommendation was endorsed by IAPSO (Resolution 1/1970) and by IUGG (Resolution 18/1971),

- notes with satisfaction the similar Recommendation put forward in 1974 by IUPAC,

- associates with IUPAC to renew the appeal to put into effect an international programme of new determinations of the absolute density of water between 0 and 40°C with an accuracy at least equal to 1 x 10^{-3} kg m^{-3},

- and recommends, meanwhile, the exclusive use of the table of the absolute density of Standard Mean Ocean Water (SMOW) between 0 and 40°C proposed by IUPAC, for the determinations of the absolute density of sea water.

(This recommendation was subsequently adopted by IAPSO and by the Plenary Session of the IUGG General Assembly in September 1975. See Annex VI)

Recommendation 2/1975

The UNESCO/ICES/SCOR/IAPSO Joint Panel of Experts on Oceanographic Tables and Standards :

- bearing in mind the ever increasing use of in situ instruments for the determination of the salinity of sea water by the measurement of conductivity;
- being aware of the rapid improvement and increased precision of such instruments during recent years;
- being also aware of the fact that a generally accepted and approved procedure for the conversion of the conductivity ratio measured at temperatures below 12 °C into the conductivity ratio contained in the International Oceanographic Tables is still lacking,
- reinforces the Recommendation 1/1973 (see attached text) of the sixth meeting of the Panel;
- stresses that accurate determinations of the temperature coefficient of the conductivity of sea water for temperatures below 12°C near to freezing point, particularly for the salinity range 32‰ to 36‰ and possibly also below 32‰, should be carried out within the next three years;
- emphasizes that such determinations should in addition be performed in the temperature range from 25° to 32°C for salinities between 36‰ and 42‰;
- urges, therefore, SCOR and IAPSO to name, through their national bodies, institutes which are prepared to undertake the determinations indicated above within the mentioned period.

ANNEX II

International Council for
the Exploration of the Sea

C.M. 1975
Hydrography Committee
C. 46

SALINOMETER INTERCALIBRATION EXPERIMENT

by
Klaus Grasshoff
Institut für Meereskunde, Kiel
and
Frede Hermann
Danmarks Fiskeri-og Havundersøgelser
Charlottenlund

In a circular letter of May 1974, the members of the Hydrography Committee and a number of other institutions were invited to participate in a salinometer intercalibration experiment.

The Standard Seawater Service (IAPSO), Charlottenlund had produced about 500 ampoules of Baltic sea water and about 900 ampoules of Mediterranean sea water. The sea water had been filtered through 0.22μ Millipore filters prior to the filling. Five ampoules of Baltic, five ampoules of Mediterranean water and four ampoules of Standard Seawater P-64 for each salinometer were distributed at cost to interested institutions. The Standard Seawater was used for standardization and check of drift of the salinometer and usually 12 measurements were made on the Baltic or Mediterranean water. The chlorinity of the Baltic and the Mediterranean water were determined by precision titration by Dr. Klaus Kremling, Institut für Meereskunde, Kiel and by Dr. Fred Culkin, Institute of Oceanographic Sciences, Wormley.

By August 1975 we had received results from 37 sets of measurements on Baltic water and 32 sets of measurements on Mediterranean water.

The reproducibility of the measurements of most of the single instruments seems to be good, at least under the circumstances under which the measurements were carried out. The 12 measurements which usually are made for each calibration seldom deviate more than 0.003 in salinity from their mean value.

The results from the different instruments, however, do deviate considerably from each other, as will appear from the following tables, where the mean value for each instrument is regarded.

Table 1 gives the results of the chlorinity titrations. Kremling's values are mean values of double titrations. Culkin's values are mean values of 14 titrations of Baltic water and 15 titrations of Mediterranean water. The standard deviations of Culkin's titrations are $8 \cdot 10^{-4}$ for the Mediterranean water and $3.6 \cdot 10^{-4}$ for the Baltic water. The two sets of titrations agree very well.

Table 1. Chlorinity titrations.

	Baltic water	Mediterranean water
Cl‰ - Culkin	4.4165	21.1025
Cl‰ - Kremling	4.415	21.103
Cl‰, Mean	4.416	21.103

The salinity S_{Cl} calculated from chlorinity using the formula in the UNESCO International Oceanographic Tables ($S_{Cl}=80655 \cdot Cl$) and the salinity S_k calculated from the old Knudsen relation ($S=1.8050 \cdot Cl+0.030$) are found in table 2 together with the mean value of all salinometer measurements and the range of these measurements.

Table 2.

	Cl‰ mean	S_{Cl}‰	S_k‰	Mean value Salinometer measurements	Range
Baltic water	4.416	7.978	8.001	8.011	8.082 to 7.976
Mediterranean water	21.103	38.124	38.121	38.125	38.140 to 38.102

The highest of the salinometer mean values, 8.17‰ for Baltic water, has been disregarded in this table and in the calculations of the following tables as the user informed us that the instrument seems to be defective.

Tables 3 and 4 show the distribution of the salinometer measurements. For the Baltic water, the distribution is far from normal; a few salinometers give far too high values.

In tables 5 and 6, the measurements are grouped after manufacturer. It is doubtful whether the values from one of the manufactures is significantly different from the values of the other manufactures.

In the tables, σ is the standard deviation round the mean values of the measurements for the manufacturer in question, σ_μ is the standard deviation of this mean value, Δ is the deviation from the mean value of all the results, as given in table 2.

Table 3. Distribution of mean values of the measurements from individual salinometers, Baltic water.

Salinity range	No. of measurements
8.09	1 (8.17)
8.090–8.086	0
8.085–8.081	1
8.080–8.076	0
8.075–8.071	1
8.070–8.066	2
8.065–8.061	0
8.060–8.056	1
8.055–8.051	1
8.050–8.046	0
8.045–8.041	1
8.040–8.036	0
8.035–8.031	0
8.030–8.026	0
8.025–8.021	2
8.020–8.016	1
8.015–8.011	0
8.010–8.006	3
8.005–8.001	6
8.000–7.996	6
7.995–7.991	5
7.990–7.986	2
7.985–7.981	3
7.980–7.976	1

Table 4. Distribution of mean values of the measurements from individual salinometers. Mediterranean water.

Salinity range	No. of measurements
38.140–38.136	3
38.135–38.131	5
38.130–38.126	8
38.125–38.121	8
38.120–38.116	5
38.115–38.111	2
38.110–38.106	0
38.105–38.101	1

Table 5. Mean values of the measurements of the individual salinometers. Baltic water S‰.

Manu-fact.	Beckman	Industria Manufact.	Autolab	Guildline	Hytech Plessey	PCC	GM 65	Switch-gear
	8.005	7.986	7.987	7.988	7.995	7.988	7.995	7.976
	8.003	7.993	7.984		7.997			
	8.003	7.985	7.992		7.999			
	8.005	8.000	8.004		8.041			
	8.082	8.020	8.010					
	8.071	8.002	7.997					
	8.006	8.022	8.021					
	8.006	8.068	8.058					
			8.054					
			8.068					
			7.984					
			7.993					
			(8.17)*					
Mean value	8.023	8.009	8.012	7.988	8.008	7.988	7.995	7.976
σ	0.033	0.027	0.031		0.024			
Δ	+ 0.012	-0.002	+0.001	0.023	-0.003			
σ_μ	0.012	0.010	0.009					
n	8	8	12	1	4	1	1	1

* This value has been disregarded.

Table 6. Mean values of the measurements of the individual salinometers. Mediterranean water S‰.

Manufact.	Beckman	Indust. Manuf.	Autolab	Guildline	NIO	Hytech	PCC1)	GM 65 2)	Switchgear
	38.126	38.124	38.134	38.132	38.124	38.118	38.129	38.128	38.123
	38.102	38.125	38.132		38.124				
	38.121	38.123	38.118						
	38.119	38.132	38.119						
	38.114	38.140	38.127						
	38.113	38.137	38.124						
	38.126	38.136	38.127						
			38.126						
			38.117						
			38.130						
			38.131						
Mean	38.117	38.131	38.126	38.132	38.124	38.118	38.129	38.128	38.123
σ	0.008	0.007	0.006						
Δ	−0.008	+0.006	+0.001	+0.007	−0.001	−0.007	+0.004	+0.003	−0.002
σ_μ	0.003	0.003	0.002						
n	7	7	11	1	2	1	1	1	1

1) PCC : "Precision Conductivity Comparator". National Oceanographic Instrument Center, U.S.A.

2) GM 65 : Inductive salinometer manufactured by "Hydrometpribor", USSR

ANNEX III

MEASUREMENT OF ABSOLUTE ELECTRICAL CONDUCTIVITY OF STANDARD SEAWATER ON THE BASIS OF KCL AS STANDARD

by Alain POISSON
Laboratoire d'Océanographie Physique, Université P. et M. Curie, PARIS

The absolute electrical conductivity χ of several batches of Standard Seawater [*] has been measured at 25°C by means of a Jones type bridge and a cell with bright platinum electrodes. The cell, with a constant geometry, has been calibrated according to the method of G. Jones and B.C. Bradshaw (1933) using a solution of KCl 0.1 Demale as a standard.

The measured conductivities thus obtained are presented in Table I (column 2). To compare these results with one another, we have adjusted them to a common base using a reference chlorinity of 19.374‰ through the relationship :

$$\chi^{25\,^\circ\mathrm{C}}_{19.374\text{‰}} = \chi^{25\,^\circ\mathrm{C}}_{\mathrm{Cl}} + \frac{\Delta\chi}{\Delta \mathrm{Cl}}\,(\mathrm{Cl} - 19.374)$$

where $\chi^{25\,^\circ\mathrm{C}}_{19.374\text{‰}}$ and $\chi^{25\,^\circ\mathrm{C}}_{\mathrm{Cl}}$ are, respectively, the absolute conductivity of sea water at 19.374‰ and at the batch chlorinity Cl‰ (Cl being very close to 19.374), $\frac{\Delta\chi}{\Delta \mathrm{Cl}}$ is the variation of conductivity of sea water per unit of chlorinity at 25°C and near 19.374‰. In our calculation, we used the ratio $\frac{\Delta\chi}{\Delta \mathrm{Cl}}$ measured by W.S. Reeburgh (1965) (see also Thomas, Thompson and Utterback, 1934).

The adjusted conductivities of the different batches (Table I, column 4) thus calculated are slightly different. As the batch P49 has a chlorinity of exactly 19.374‰ (i.e., 35.000‰ in salinity), we took it as reference. The difference of adjusted conductivities with P49 are then converted into equivalent of chlorinity ΔCl (Table I, column 5).

The accuracy of our results is limited by the accuracy of measurement of temperature and of resistance. As the temperature of the sample is measured with an accuracy of $\pm$ 0.001°C, and as the variation of conductivity of sea water with temperature is about 0.02 of the conductivity value per degree Celsius, the error due to temperature can be estimated to be $\pm 2\cdot10^{-5}$ of the conductivity. The error on the measured resistance is estimated to be $\pm 1\cdot10^{-5}$ of its value. Then the accuracy of conductivity is $\pm 3\cdot10^{-5}$ of its value, that is, $1.6\,\mu\Omega^{-1}\mathrm{cm}^{-1}$ for Standard Seawater at 25°C. In comparison, the chlorinity of various batches is known with an accuracy of $\pm$ 0.001‰, which is equivalent, at 25°C, to a variation of $2.4\,\mu\Omega^{-1}\mathrm{cm}^{-1}$ in conductivity.

---

[*] Standard Seawater of the Standard Seawater Service (now located at the Institute of Oceanographic Sciences, Wormley, United Kingdom) is used as the reference in salinometers against which the electrical conductivity of sea water samples is calibrated as a measure of the chlorinity.

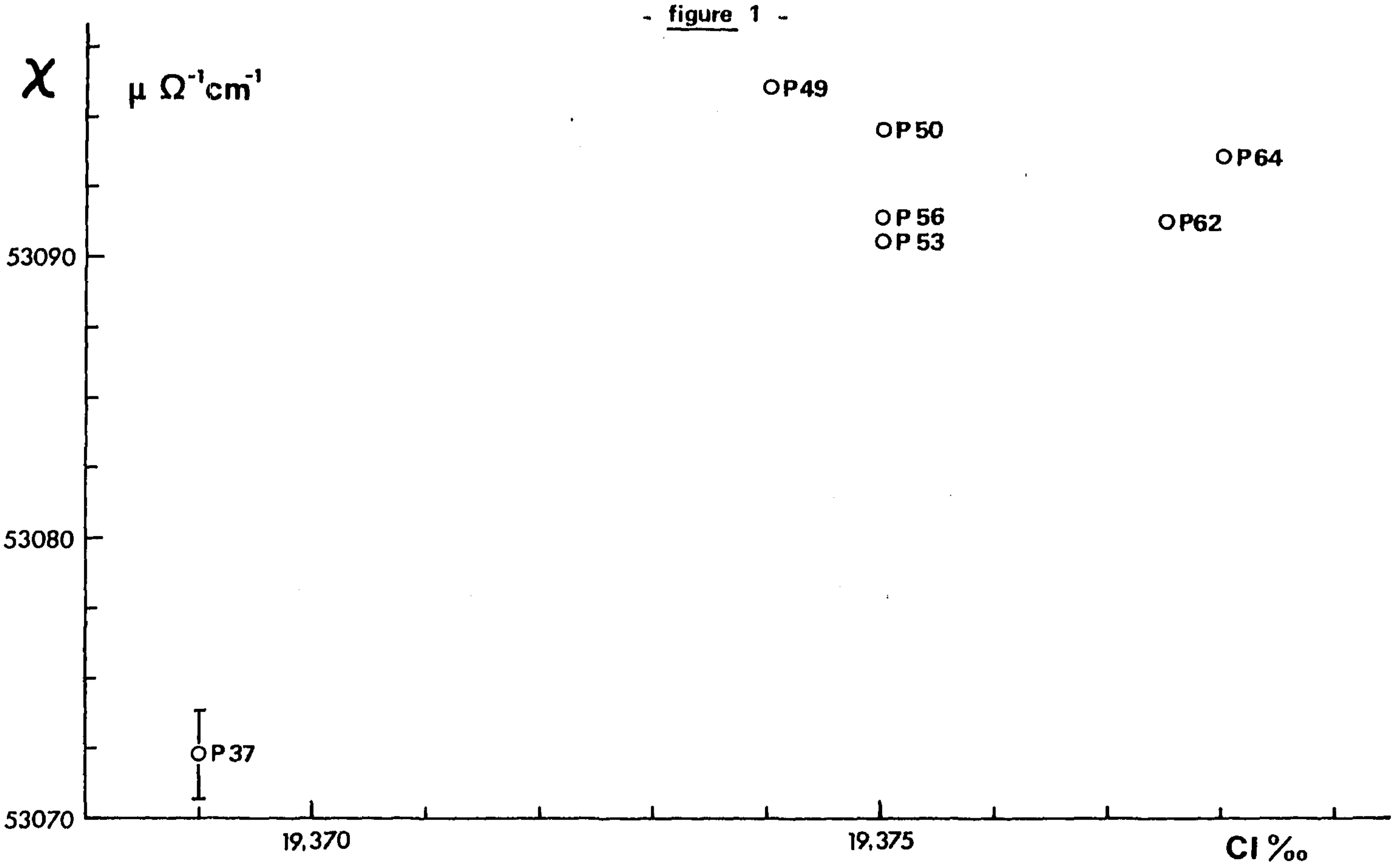
The measurements on different ampoules of the same batch P64 show on one hand, that the reproducibility of the method is excellent, and on the other hand that the conductivity of sea water of any one batch is constant, within the limits of accuracy of our method. But the differences measured between different batches cannot be explained by experimental error. They vary in an unpredictable way relative to their chlorinity (figure 1) or their age (figure 2). This presents a problem concerning the calibration of Standard Seawater in terms of absolute conductivity, because the above results indicate that the electrical conductivity is not simply a function of the sea water chlorinity.

TABLE I *

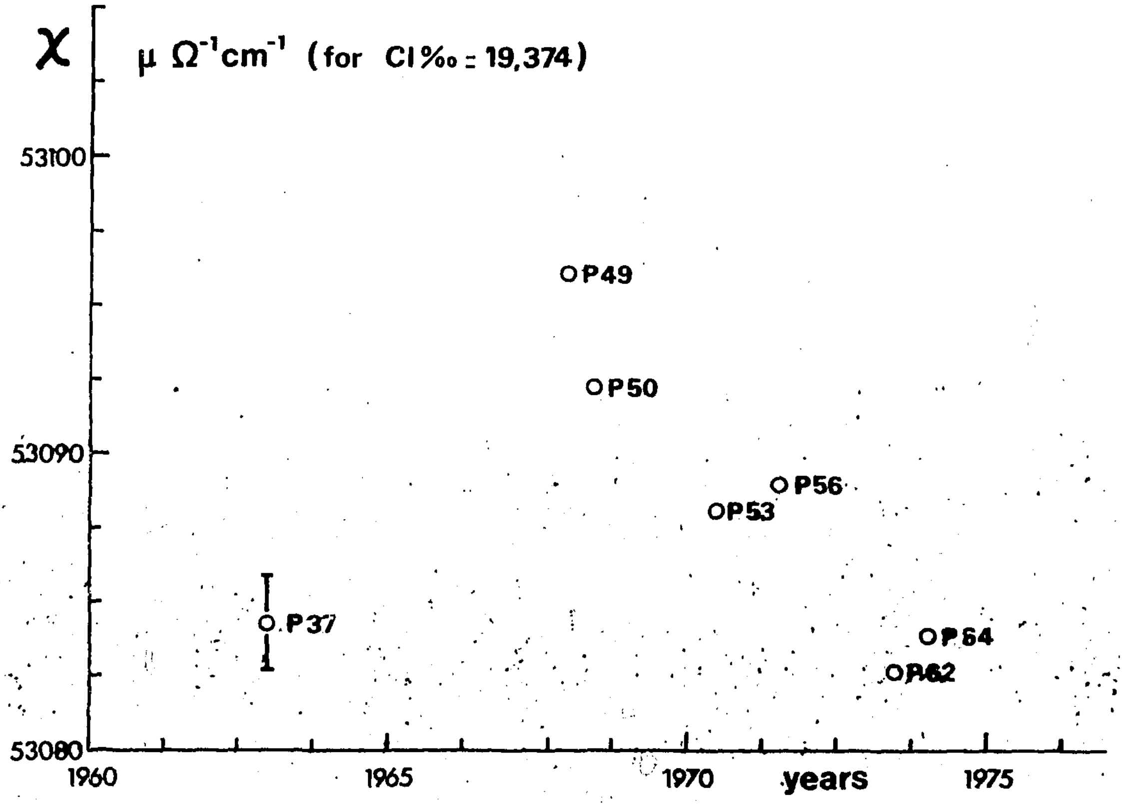
1	Measured conductivity 2			Measured chlorinity 3	Adjusted conductivity 4	Difference of adjusted equivalent chlorinity relative to 19.374°/oo 5
Batch	$\chi_{Cl}^{25°C}$ $\mu\Omega^{-1}cm^{-1}$			Cl°/oo °/oo	$\chi_{19.374°/oo}^{25°C}$ $\mu\Omega^{-1}cm^{-1}$	Δ Cl 10^{-3} °/oo
P 64-1 P 64-1	53094.4 53095.1	) 53094.7	53093.6	19.378	53083.9	-5.0
P 64-2 P 64-2	53092.7 53093.1	) 53092.9				
P 64-3 P 64-3	53093.7 53093.9	) 53093.8				
P 64-4 P 64-4	53092.2 53091.8	) 53092.0				
P 64-5 P 64-5	53094.7 53094.7	) 53094.7				
P 62-1 P 62-1	53091.5 53091.0	) 53091.2		19.3775	53082.7	-5.5
P 56-1 P 56-1	53090.3 53092.5	) 53091.4		19.375	53089.0	-2.9
P 53-1 P 53-1	53090.3 53090.8	) 53090.5		19.375	53088.1	-3.3
P 50-1 P 50-1	53093.6 53095.5	) 53094.5		19.375	53092.1	-1.6
P 49-1 P 49-1	53096.3 53095.8	) 53096.0		19.374	53096.0	0
P 37-1 P 37-1	53072.2 53072.5	) 53072.3		19.369	53084.5	-4.7

* χ 25°C = absolute conductivity of seawater at 25 °C
accuracy = 1.6 $\mu\Omega^{-1}$ cm^{-1}

- figure 1 -



- figure 2 -



REFERENCES

Jones, G.; Bradshow, B.C. 1933. The measurement of the conductance of electrolytes. V. A Redetermination of the Conductance of Standards Potassium Chloride Solutions in Absolute Units. J. Amer. Chem. Soc., Vol. 55, p. 1780-1800.

Park, K. 1964. Reliability of Standard Seawater as a Conductivity Standard. Deep Sea Research, Vol. 11, p. 85-7.

Reeburgh, W.S. 1965. Measurements of the Electrical Conductivity of Seawater. J. Mar. Res. Vol. 23, p. 187-199.

Thomas, D.; Thompson, T.G.; Utterback, C.L. 1934. The Electrical Conductivity of Seawater. J. Conseil, Conseil Perm. Intern. Explor. Mer, Vol. 9, p. 28-35.

Weyl, P.K. 1964. On the Change in Electrical Conductance of Seawater with Temperature. Limnol. and Oceanog., Vol. 9, p. 75-8.

ANNEX IV

LETTER TO EDITOR

On the problem of future replacement of Knudsen-Ekman's equation of state of sea water

(Statement of problems and invitation for comments)

During the meeting of the UNESCO/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards (Grenoble, 2 - 5 September 1975) it was decided to solicit reactions and comments to the proposal that a new equation should replace the Knudsen-Ekman equation of state of sea water. This communication is designed to raise any comments on this proposal that may help the Panel in formulating its decision at its next meeting in early 1977.

As is well known, hitherto the equation of state of sea water has been based on the works of Knudsen (1901), Forch et al. (1902) and Ekman (1908), whose formulae and tables of the density of sea water and related function are used exclusively in oceanographic research. Recent works by Cox, McCartney, and Culkin (1970), Kremling (1972), and Millero, Gonzalez and Ward (1975) have indicated that there exist a mean systematic difference between these and Knudsen's data of $(8.7 \pm 1.0) \times 10^{-6} cm^3 \cdot g^{-1}$ over the entire ocean temperature range at a salinity of 35‰ in the specific volume. It should be emphasized that while this difference is systematic, the precision of the Knudsen tables is of order of $1 \cdot 10^{-1} cm^3 \ g^{-1}$. Table 1 summarises the differences for 35‰ salinity sea water

Table 1:

Comparison of specific volume data between new measurements and Knudsen (1901) data for S = 35 ‰ sea water

Temperature °C	Specific volume x 10^6 (new minus Knudsen) $cm^3 \ g^{-1}$
0	7
5	8
10	10
15	10
20	9
25	8
	mean 8.7 ± 1

The data for specific volume under pressure of Ekman (1908), extrapolated beyond 600 bars pressure, appear to be in error by as much as $(89 \pm 5) \cdot 10^{-6} cm^3 \cdot g^{-1}$ at 35‰ salinity at 1000 bars (Table 2), if compared with the more recent data of Bradshaw and Schleicher (1975), Chen and Millero (1975) and Fine, Wang and Millero (1974), Wang and Millero (1973). The latter publications arrived at the same differences from the Ekman results by different techniques within the above stated precision.

It should be pointed out that although a large volume error exists at high pressures, the pressure dependence of the coefficient of thermal expansion is not altered by more than 5×10^{-6} cm$^3 \cdot g^{-1}$ °C^{-1}.

Table 2.

Comparison of the specific volumes between new measurements and Ekman (1908) values for S = 35‰ sea water at 0°C.

Pressure bars	Specific volume x 10^6 (new minus Ekman) cm$^3 \cdot g^{-1}$
0	0
100	18
200	28
300	32
400	33
500	33
600	34
700	38
800	48
900	64
1000	89

The equation of state of sea water under consideration will yield precisions of specific volumes of 3×10^{-6} cm$^3 \cdot g^{-1}$ at 1 bar and 5×10^{-6} cm$^3 \cdot g^{-1}$ at 1000 bars at 35‰ S.

The Joint Panel is also of the opinion that over the major salinity range of the World Ocean (33-37) ‰, salinities obtained by conductivity determinations using various recent conductivity equations can be directly used for computation of density with the new equation of state. At salinity values below and above this range, salinities obtained from the UNESCO conductivity salinity conversion tables (Unesco, 1971) can be slightly different because of minor compositional changes in sea water (ref., e.g., Kremling, 1972). This matter is presently under intensive investigation. The future equation of state is mostly based on the work of Chen and Millero (1975), and Millero, Gonzalez, and Ward (1975) and is valid over the oceanic salinity range of 33-37‰ using salinity values obtained by conductivity techniques, but will be equally valid over the entire range of salinities as soon as appropriate corrections can be made to salinities derived from the UNESCO conductivity salinity conversion tables.

The Joint Panel invites comments and reactions from oceanographers and associated explorers throughout the world with regard to the proposal for the future replacement of the Knudsen-Ekman equation of state by a new equation of state. Knowledge of these opinions is very essential before any firm proposals will be made by the Joint Panel at its next meeting in early 1977.

Comments should be sent to the Chairman of the Joint Panel (address below).

Professor Dr. Klaus Grasshoff
Marine Chemistry Department
Institut für Meereskunde an der
Universität Kiel,
D-23 Kiel,
Düsternbrooker Weg 20,
Federal Republic of Germany

REFERENCES

Bradshaw, A.; Schleicher, K.E. 1975. Deep Sea Res. (in press)

Chen, C.T.; Millero, F.J. 1975. The specific volume of sea water at high pressures. Deep Sea Res. (in press)

Cox, R.A.; McCartney, M.J.; Culkin, F. 1970. The specific gravity/salinity/temperature relationship in natural sea water. Deep Sea Res., Vol. 17, p. 679-89.

Ekman, V.W. 1908. Die Zusammendrückbarkeit des Meerwassers nebst einigen Werten für Wasser und Quecksilber. Publications de Circonst., Vol. 43, p. 1-47.

Fine, R.A.; Wang, D.P.; Millero, F.J. 1974. The equation of state of sea water. J. Mar. Res., Vol. 32, p. 433-56.

Forch, C.; Knudsen, M.; Sörensen, S.P.L. 1902. Berichte über die Konstantenbestimmungen zur Aufstellung der Hydrographischen Tabellen. D. Kge. Danske Vidensk. Gelsk. Skriftar 6. Raekke, naturvidensk. og mathem. Afel. XII, 1.

Knudsen, M.H.C. 1901. Hydrographische Tabellen. G.E.C. Goad Copenhagen.

Kremling, K. 1972. Comparison of specific gravity in natural sea water from hydrographic tables and measurements by a new density instrument. Deep Sea Res., Vol. 19, p. 377-83.

Kremling, K. 1972. Untersuchungen über die chemische Zusammensetzung des Meerwassers aus der Ostsee. III Frühjahr 1969-Herbst 1970. Kieler Meeresforsch. Vol. 28, p. 99-118.

Millero, F.J.; Gonzalez, A.; Ward, G.K. 1975. The density of sea water solutions at one atmosphere as a function of temperature and salinity. J. Mar. Res. (in press).

Unesco, 1971. International Oceanographic Tables Vol. 1.

Wang, D.P.; Millero, F.J. 1973. Precise representation of the P-V-T. properties of water and sea water determined from sound speeds. J. Geophys. Res., Vol. 78, p. 7122-8.

ANNEX V

TABLE OF ABSOLUTE DENSITY OF STANDARD MEAN OCEAN WATER (SMOW) AS A FUNCTION OF TEMPERATURE FROM 0°C TO 40°C.

by Maurice Menaché

The absolute density of SMOW, ρ(SMOW), free from dissolved atmospheric gases and under a pressure of 101 325 Pa (one standard atmosphere) is given in kilogrammes per cubic meter (kg m^{-3}) as a function of temperature in the table annexed. This table was prepared by Commission I.4 on Physicochemical Data and Standards of the International Union of Pure and Applied Chemistry (IUPAC), which recommends its exclusive use until sufficiently accurate new determinations have been made.

Its universal use presents the two following advantages :

1. It provides a single basis for the comparisons of all precise measurements of volume or absolute density. The results achieved could be corrected later when relevant values of the absolute density of water are obtained.

2. It draws attention to the isotopic composition of the sample of water under consideration, and enables the influence of this composition to be taken into account in the calculation.

The following explanation is useful concerning this table.

SMOW (Standard Mean Ocean Water) is a pure water obtained from the ocean, constituting the universal isotopic standard. This was proposed and prepared by Craig (1961) and is kept by the International Atomic Energy Agency, which is responsible for its distribution in small quantities (about 25 cm^3) to laboratories specialized in isotopic water analysis. It is recommended that SMOW should be used as reference when calculating results of precise absolute density determinations.

The maximum absolute density of SMOW, ρ_{max}(SMOW), at a pressure of one standard atmosphere and in the absence of dissolved atmospheric gases, which occurs at a temperature close to 4°C, has a provisionally accepted value (Girard and Menaché, 1972) equal to 999.975 kg m^{-3}.

The isotopic composition of any given sample of water is usually determined by comparison with SMOW, using mass spectrometry. The results of this comparison are expressed by the relative differences δ_{18} and δ_D, which are defined in the following relations :

$$\delta_{18} = \frac{[18_O]/[16_O]\ (\text{Sample}) - [18_O]/[16_O]\ (\text{SMOW})}{[18_O]/[16_O]\ (\text{SMOW})} \times 10^3$$

$$\delta_D = \frac{[D]/[H]\ (\text{Sample}) - [D]/[H]\ (\text{SMOW})}{[D]/[H]\ (\text{SMOW})} \times 10^3$$

where $[^{18}O]/[^{16}O]$ and $[D]/[H]$ are the ratios of the molar concentrations of these different nuclides in the sample.

The values for SMOW are :

$$[^{18}O]/[^{16}O] = (1993.4 \pm 2.5) \times 10^{-6} \text{ (Craig, 1961)}$$

$$[D]/[H] = (155.76 \pm 0.05) \times 10^{-6} \text{ (Hagemann et al., 1970)}$$

The annexed table of recommended values for the absolute density of SMOW is based on that presented by Bigg (1967) (see also Wagenbreth and Blanke, 1971). Values calculated by the relation

$$\rho(\text{SMOW})/(\text{kg m}^{-3}) = \rho(\text{Bigg}) \times 999.975/999.972 \qquad (1)$$

were fitted within 1×10^{-4} kg m^{-3} by the following equation from which the table was generated :

$$\rho(\text{SMOW})/(\text{kg m}^{-3}) = a_o + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 \qquad (2)$$

where $a_o = 999.842\,594$; $a_1 = 6.793\,952 \times 10^{-2}\,°\text{C}^{-1}$;

$a_2 = -9.095\,290 \times 10^{-3}\,°\text{C}^{-2}$; $a_3 = 1.001\,685 \times 10^{-4}\,°\text{C}^{-3}$;

$a_4 = -1.120\,083 \times 10^{-6}\,°\text{C}^{-4}$; $a_5 = 6.536\,332 \times 10^{-9}\,°\text{C}^{-5}$.

If the precise absolute density ρ of a given sample of water is required at a temperature t expressed on the International Practical Temperature Scale of 1968, it is first of all necessary to determine the isotopic composition of the sample, then to calculate the δ_{18} and δ_D values, and finally to apply an isotopic density correction to the appropriate value of ρ(SMOW) taken from the annexed table.

The isotopic density correction may be determined from the following provisional relationship which has been obtained from experiments by Girard and Menaché (1971).

$$\left[\rho(\text{sample}) - \rho(\text{SMOW})\right] \times (10^3/\text{kg m}^{-3}) = 0.211\ \delta_{18} + 0.015\,0\ \delta_D \qquad (3)$$

When using the annexed table and equation (3), the following reservations should be taken into account (Menaché and Girard, 1973).

1. Equation (2), which is the basis used for calculating the values given in the table, is derived from the combined observations of the dilatation of water, made by Chappuis (1907) and by Thiesen (1900). These measurements were made at the beginning of the century. The two groups of results show differences which increase in magnitude with rise in temperature and which become relatively appreciable at temperatures above 16°C. The annexed table is consequently proposed as a provisional standard until such time as sufficiently precise new determinations have been made.

2. It is not yet possible to fix an accurate value of the absolute density of a sample of water of well defined isotopic composition. The value of ρ_{max} (SMOW) = 999.975 kg m^{-3}, which enters into the calculation of the values given in the table, shows a slight uncertainty which we estimate to be limited to approximately 3 x 10^{-3} kg m^{-3}. This value may be subject to a small modification when sufficiently accurate results of new absolute determinations become available.

3. Equation (3), which is proposed for calculating the isotopic correction, is applicable only for natural waters. It does not apply to artificial waters prepared or appreciably altered in composition in the laboratory. It is the result of a relatively limited number of observations, and therefore, is also of a provisional nature. New determinations (Girard and Menaché, 1975) made in greater number with an improved precision show that it should be slightly amended. This amendment will not, however, be proposed until a later date when the new results may be compared with others obtained in other laboratories. The limit of the error introduced by the use of equation (3) may be estimated for the water samples generally used in laboratory at about 1 x 10^{-3} kg m^{-3}. In order to reduce this error, it is recommended that, whenever possible, observations should be carried out on samples of water that have as close a composition as possible to that of SMOW. This can be achieved by purifying ocean water. The isotopic composition of these samples must, nevertheless, be determined by mass spectrometry.

REFERENCES

Bigg, P. H. 1967. Density of water in SI units over the range 0-40 °C. British Journ. Applied Physics, Vol. 18, p. 521-5, (table p. 523).

Chappuis, P. 1907. Dilatation de l'eau. Travaux et Mémoires du Bureau International des Poids et Mesures, Vol. 13, pages D1 à D40 (table p. D40).

Craig, H. 1961. Standards for reporting concentrations of Deuterium and Oxygen-18 in natural waters. Science, Vol. 133, p. 1833-4.

Girard, G.; Menaché, M. 1971. Variation de la masse volumique de l'eau en fonction de sa composition isotopique. Metrologia, Vol. 7, n° 3, July 1971, p. 83-7.

Girard, G.; Menaché, M., 1972. Sur le calcul de la masse volumique de l'eau. Compte Rendu de l'Académie des Sciences, Paris, série B, tome 274, p. 377-9.

Girard, G.; Menaché, M., 1975. Nouvelles mesures de la masse volumique de l'eau en fonction de sa composition isotopique. Paper given at the Symposium "Thermodynamics of the Sea and Equation of State", XVIth General Assembly of the International Association of the Physical Sciences of the Ocean, Grenoble, France, 25 August - 6 September 1975.

Hagemann, R.; Nief, G.; Roth, E. 1970. Absolute isotopic Scale for Deuterium analysis of natural waters. Absolute D/H ratio for SMOW. Tellus, Vol. 22, n°6, p. 712-5.

Menaché, M.; Girard, G. 1973. Concerning the different Tables of the Thermal Expansion of Water between 0 and 40°C. Metrologia, Vol. 2, p. 1962-8.

Thiesen, M. 1900. Untersuchungen über die thermische Ausdehnung von festen und tropfbarflüssigen Körpern, ausgeführt durch M. Thiesen, K. Scheel und H. Diesselhorst. Wissenschaftlische Abhandlungen der Physikalisch-Technischen Reichanstalt, Vol. 3, page 1-70 (table p. 68).

Wagenbreth, H.; Blanke, W. 1971. Die Dichte des Wassers im Internationalen Praktischen Temperatureskala von 1968. P.T.B. - Mitteilungen 6/71, p. 412-5 (formula 6).

ERRATUM : this table should be inserted following Annex V (page 35)

Absolute Density of Standard Mean Ocean Water (SMOW) ρ/kg m^{-3} free from dissolved atmospheric gases, at a pressure of 101 325 Pa for temperatures t/°C on the International Practical Temperature Scale of 1968

	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	999.8426	8493	8558	8622	8683	8743	8801	8857	8912	8964
1	999.9015	9065	9112	9158	9202	9244	9284	9323	9360	9395
2	999.9429	9461	9491	9519	9546	9571	9595	9616	9636	9655
3	999.9672	9687	9700	9712	9722	9731	9738	9743	9747	9749
4	999.9750	9748	9746	9742	9736	9728	9719	9709	9696	9683
5	999.9668	9651	9632	9612	9591	9568	9544	9518	9490	9461
6	999.9430	9398	9365	9330	9293	9255	9216	9175	9132	9088
7	999.9043	8996	8948	8898	8847	8794	8740	8684	8627	8569
8	999.8509	8448	8385	8321	8256	8189	8121	8051	7980	7908
9	999.7834	7759	7682	7604	7525	7444	7362	7279	7194	7108
10	999.7021	6932	6842	6751	6658	6564	6468	6372	6274	6174
11	999.6074	5972	5869	5764	5658	5551	5443	5333	5222	5110
12	999.4996	4882	4766	4648	4530	4410	4289	4167	4043	3918
13	999.3792	3665	3536	3407	3276	3143	3010	2875	2740	2602
14	999.2464	2325	2184	2042	1899	1755	1609	1463	1315	1166
15	999.1016	0864	0712	0558	0403	0247	0090	9932*	9772*	9612*
16	998.9450	9287	9123	8957	8791	8623	8455	8285	8114	7942
17	998.7769	7595	7419	7243	7065	6886	6706	6525	6343	6160
18	998.5976	5790	5604	5416	5228	5038	4847	4655	4462	4268
19	998.4073	3877	3680	3481	3282	3081	2880	2677	2474	2269
20	998.2063	1856	1649	1440	1230	1019	0807	0594	0380	0164
21	997.9948	9731	9513	9294	9073	8852	8630	8406	8182	7957
22	997.7730	7503	7275	7045	6815	6584	6351	6118	5883	5648
23	997.5412	5174	4936	4697	4456	4215	3973	3730	3485	3240
24	997.2994	2747	2499	2250	2000	1749	1497	1244	0990	0735
25	997.0480	0223	9965*	9707*	9447*	9186*	8925*	8663*	8399*	8135*
26	996.7870	7604	7337	7069	6800	6530	6259	5987	5714	5441
27	996.5166	4891	4615	4337	4059	3780	3500	3219	2938	2655
28	996.2371	2087	1801	1515	1228	0940	0651	0361	0070	9778*
29	995.9486	9192	8898	8603	8306	8009	7712	7413	7113	6813
30	995.6511	6209	5906	5602	5297	4991	4685	4377	4069	3760
31	995.3450	3139	2827	2514	2201	1887	1572	1255	0939	0621
32	995.0302	9983*	9663*	9342*	9020*	8697*	8373*	8049*	7724*	7397*
33	994.7071	6743	6414	6085	5755	5423	5092	4759	4425	4091
34	994.3756	3420	3083	2745	2407	2068	1728	1387	1045	0703
35	994.0359	0015	9671*	9325*	8978*	8631*	8283*	7934*	7585*	7234*
36	993.6883	6531	6178	5825	5470	5115	4759	4403	4045	3687
37	993.3328	2968	2607	2246	1884	1521	1157	0793	0428	0062
38	992.9695	9328	8960	8591	8221	7850	7479	7107	6735	6361
39	992.5987	5612	5236	4860	4483	4105	3726	3347	2966	2586
40	992.2204									

ANNEX VI

IUGG Resolution XVI (adopted 6 September 1975)

THE INTERNATIONAL UNION OF GEODESY AND GEOPHYSICS

NOTING the resolutions of IAPSO and the UNESCO/IAPSO/SCOR/ICES Joint Panel of Experts on Oceanographic Tables and Standards,

ENDORSES the recommendation put forward in 1974 by IUPAC, in favour of an international programme of new determinations of the absolute density of water between 0 and 40°C with an accuracy at least equal to 1×10^{-3} kg m^{-3}, and

RECOMMENDS, meanwhile, the exclusive use of the table of the absolute density of SMOW between 0 and 40°C proposed by IUPAC, for the determinations of the absolute density with reference to pure water.

APPENDIX I

NS/9/114B.
Paris, 4 December 1962.

UNITED NATIONS EDUCATIONAL
SCIENTIFIC AND CULTURAL ORGANIZATION

REPORT OF JOINT PANEL ON THE EQUATION OF STATE OF SEA WATER

Introduction

It has been a matter of concern to many oceanographers that our knowledge of the physical and chemical properties of sea water is inadequate. The recent development of instruments capable of measuring a property of sea water with precision of more than an order of magnitude greater than previously possible, has created a situation where the functional relationships between the measured property and other properties which at present are difficult to measure directly, limit the use of the new techniques. Specifically, the electrical conductivity of a sample of sea water can be measured with a precision in the part per million range. The purpose of measuring conductivity is not to obtain a measure of that property per se but to provide an indirect measure of density, a property needed in studies of the hydrodynamics of the oceans, and of chlorinity and salinity, two properties that have been used in the description of the oceans for over fifty years. The relationships between conductivity and density, chlorinity and salinity are not known with a precision comparable to that of measured conductivity values.

These matters were discussed at length at the conference on physical and chemical properties of sea water at Easton, Maryland, in September 1958. (Pub. 600, Nat. Acad. of Sciences, Nat. Research Council).

Two years ago the National Institute of Oceanography in England initiated a programme for the collection of water samples from all parts of the world, and investigation of their physical and chemical properties. This programme was supported by the International Council for the Exploration of the Sea, and by the Office of Oceanography of Unesco which made a cash grant to cover some of the expenses of the collection of the samples.

The first results of this programme were reported to the ICES Hydrographic Committee at the 49th Statutory Meeting at Copenhagen, October 1961 (Cox, Culkin and Riley, 1961) and later published (Cox, Culkin, Greenhalgh and Riley, 1962). These results indicate that the relationships currently accepted between chlorinity and density are inadequate, and that while there is a reasonably constant relationship between conductivity and density there is a much wider variation in the chlorinity to density relationship. It was decided at the ICES meeting that we must face the possibility of abandoning the definition of "salinity" in terms of chlorinity which has been generally accepted since it was recommended by Knudsen in 1902. (Knudsen, Forch and Sørensen, 1902). It was now apparent that more precise estimates of water density could be obtained by measuring the conductivity. If the term "salinity" was to be retained, as a convenient means of describing a particular water, then it must be redefined in terms of conductivity or density.

The Hydrographical Committee of ICES decided that these were matters of concern to all oceanographers, and that it would be best to organize a group similar to the Commission presided over by Knudsen in 1901 to draw up recommendations on the best procedure. ICES called on SCOR and IAPO to join in appointing a suitable group of experts, and Unesco undertook to finance and organize the meeting. The following resolution was adopted by the Hydrographical Committee of ICES at its 49th Statutory Meeting and passed by the Council:

"The Hydrographical Committee recommends, as a consequence of the introduction of the conductivity method as a standard method for the determination of salinity, that the Council should submit the following recommendations to Unesco :

i) That the ICES, the IAPO, the SCOR and any other international oceanographic bodies deemed appropriate, be requested (a) to review present knowledge of the equations of state of sea water, in particular of the properties of chlorinity, salinity, density, conductivity and refraction index, and the relationship among these properties, (b) to consider whether re-definition of any of these properties is necessary, and (c) to advise on such further investigations as may be required,

ii) That the Unesco Office of Oceanography be asked to provide the funds necessary for implementation of the above recommendations."

In response to this recommendation, Unesco organized a Joint Panel on the Equation of State of Sea Water, whose members were nominated by ICES, IAPO, SCOR, and Unesco. This panel met at Unesco Headquarters, Paris, on 23 to 25 May 1962.

The Panel consists of the following members :

Professor D.E. Carritt IAPO
Department of Geology and Geophysics
Massachusetts Institute of Technology
Cambridge, 39, Massachusetts, U.S.A.

Dr. R.A. Cox ICES
National Institute of Oceanography
Wormley, Surrey, England

Professor Dr. G. Dietrich SCOR
Institut für Meereskünde
Hohenbergstrasse 2,
Kiel, FRG

Dr. N.P. Fofonoff IAPO
Pacific Oceanographic Group
Nanaimo, British Columbia, Canada

Mr. F. Hermann ICES
Danmarks Fiskeri-og Havundersøgelser
Charlottenlund Slot
Charlottenlund, Denmark

Dr. G.N. Ivanoff-Frantzkevich UNESCO
Institute of Oceanology
Academy of Sciences
Bakrushina 8
Moscow J-127, USSR

Dr. Y. Miyake SCOR
Meteorological Research Institute
Mabashi, Suginami-ku
Tokyo, Japan

At the May 1962 meeting Professor Dietrich was elected chairman and Professor Carritt rapporteur. All members of the Panel were present. Also present were the following observers :

Dr. K.N. Fedorov (UNESCO)
Professor Lacombe (France)
Dr. B. Saint-Guily (France)
Dr. Y. Takenouti (UNESCO)
Dr. P. Tchernia (France)
Dr. W.S. Wooster (UNESCO)

Summary of Cox Measurements

Measurements of physical and chemical properties of sea water made by Cox and his co-workers at NIO provided much of the impetus behind the formation of the Joint Panel. Dr. Cox was asked to summarize the results of his studies, especially those obtained subsequent to the last published report. (Cox *et al.* 1962).

Cox reported that the published results included values primarily in the salinity range 34 - 35‰ . New values augment the previous measurements and extend the range to include waters of salinity 33-39‰ . The conclusions to be reached from the data now at hand are in general the same as previously reported.

At present approximately 300 samples have been analyzed for chlorinity and relative conductivity. Of these approximately 120 have been analyzed for relative density. The geographic distribution of samples is shown in fig. I.

The conductivity measurements have been made relative to Copenhagen Standard Sea Water. Two batches of Standard Water were used and intercomparison of the chlorinity to conductivity ratio showed their properties to be essentially identical. Precise chlorinity determinations were made by the method described by Bather and Riley (1953).

Density has been reported in arbitrary units. Determinations of absolute conductivity and absolute density will shortly be made.

A large scale plot of all the chlorinity - relative conductivity data (approximately 300 measures) was examined by the Panel. A part of the curve is shown in Fig. 2. It was pointed out that if the measured value of one of these properties is to be used as a basis for predicting the other, the measured values of both properties must fall on a smooth curve. They do not. Visual examination of the data showed that for two waters of the same conductivity the chlorinity may vary by as much as 0.03‰. This is interpreted as demonstrating the failure of the constancy of relative properties of dissolved constituents in sea water. In addition, it was noted that for waters of the same chlorinity, deep samples (below 1000m) tend to have a higher relative conductivity than shallow samples.

A plot of relative density *vs* chlorinity (approximately 120 measures), a part of the data is given in fig. 3, shows much the same scatter as in the chlorinity - relative conductivity data. Two waters having the same density may differ by as much as 0.025‰ in chlorinity.

A plot of relative density *vs* relative conductivity shows much less scatter than either the chlorinity - relative conductivity or relative density *vs* chlorinity plots. The mean deviation from a visually fitted curve is approximately 0.005‰ in equivalent salinity. Samples showing the greatest departure from the mean curve were a few deep samples and a few surface samples from high latitudes. A part of the data are shown in figure 4.

The panel discussed the significance of these findings relative to present tabulated values of the same properties, the uses of measured values of the properties and quantities derived from them, and was especially concerned with possible contradictions of existing notions and concepts implicit in conclusions drawn from the new data.

It was noted that measurements made by techniques capable of high precision and accuracy are used to obtain an indirect estimate of *in situ* density, which in turn is required in geostrophic computations, estimates of stability, etc.

Estimation of In Situ Density

Classically the method of estimating *in situ* density has involved the following stops :

1. Measurements of chlorinity (by Knudsen titration) of a sample of sea water of known *in situ* temperature and pressure and estimation of σ_0 using Knudsen's tables. The relationship between Cl‰ and σ_0 derived by Knudsen was based upon the measurement of chlorinity and density on twenty four surface samples, only twelve of which had chlorinities in the range 15 to 21‰. Although Knudsen (Knudsen, Forch and Sørensen, p. 158) pointed out that the difference between measured and computed values of σ_0 was as much as 0.01 in σ_0, neither tabulated values nor the analytical expression between Cl‰ and σ_0 contain an indication of the precision and accuracy to be expected.

2. Estimation of density under in situ conditions by modifying σ_0 by expressions which take into account the thermal expansion coefficient and the compressibility of sea water. Since all of Cox's measurements were made at 0°C and atmospheric pressure, these computations were not discussed in detail. It was noted, however, that neither the coefficient of thermal expansion nor the compressibility are known with a precision comparable to that of Cox's measurements of relative density or relative conductivity.

Knudsen's Tables list values for chlorinity in intervals of 0.01‰ along with corresponding values of σ_0. Depending upon the absolute value of chlorinity, each 0.01‰ change in chlorinity corresponds to a change of σ_0 of 0.01 to 0.03 units. The implication here is that if the second decimal in chlorinity is established with certainty, the predicted value of σ_0 will be certain in the second decimal. However, Cox has clearly shown that for a given value of σ_0 (expressed by Cox as relative density), chlorinity may vary from sample to sample by at least 0.03‰. In other words, measured values of chlorinity do not provide a precise means of estimating density or σ_0.

Cox's measurements clearly demonstrate that the use of the functional relationship between chlorinity and density (σ_0) as derived by Knudsen and tabulated in Knudsen's Tables yields ambiguous results when used to predict σ_0 from measured values of chlorinity. In addition, his measurements point to a satisfactory alternative. The plot of relative density vs relative conductivity (fig. 4) indicates that a functional relationship between σ_0 and electrical conductivity can be obtained which will provide the means of predicting more precise and accurate values of σ_0 from measured values of conductivity, than can be obtained from chlorinity and the Knudsen procedure. It should be emphasized that this is so because of inherent properties of sea water and not merely because routine measurements of conductivity can now be made with greater accuracy, precision (and speed) than can be achieved for chlorinity determination by the Knudsen titration.

In the case of both density and electrical conductivity, Cox's measurements are in terms of arbitrary references. Conductivity measurements have all been referred to Copenhagen Standard Sea Water which at the present time has only been standardized with reference to chlorinity. It is now clear that as soon as is practicable, Standard Water also must be certified with regard to conductivity. Because of the obvious practical importance of this property, the primary reference for sea water should be the international ohm. Cox has already designed and is having built equipment which will provide measurements in terms of standard units of length and resistance. The measurement of a few of the samples now reported in relative terms will provide the basis for conversion of all of the data to an absolute basis.

Similarly, Cox's density data are now in relative terms which he will convert to absolute units (gm/cm^3) by precise pycnometric measurement of several of the samples already measured in relative units.

Salinity

Salinity has a unique place among the properties used to describe sea water - it is one of the most commonly used terms yet it is never measured directly. As far as can be discovered only nine direct measurements of salinity have been made, they being the ones reported by Forch, Knudsen and Sørensen (1902).

Originally Sørensen (loc cit.) defined salinity as : "the total amount of solid material in grams contained in one kilogram of sea water, when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine and all organic matter completely oxidized."

Knudsen (loc. cit., p. 156) used the nine direct measures of salinity together with corresponding chlorinity values and calculated the familiar relation :

(1) $$S‰ = 0.030 + 1.805\ Cl‰$$

and pointed out that the differences between computed and measured values of S ‰ were probably due to differences in the composition of the dissolved salts in the samples examined.

Because of the technical difficulties associated with measuring salinity according to the Sørensen definition, Knudsen proposed that salinity be defined by equation (i).

It has also been pointed out by Carritt and Carpenter (1959) that the uncertainty of a computed value of salinity from a measured value of chlorinity, using equation (1) is as much as 0.04‰ , this being inherent in the composition of sea water and not the result of analytical error. This in itself is sufficient reason to suggest that the use of salinity, where it implies grams of solids per kilogram of sea water, or the property defined by Sørensen, does not have the precision and accuracy inherent in the Knudsen chlorinity titration and certainly is much inferior to that obtainable by present day conductivity measurements and direct measurements of density.

It should be borne in mind that neither the Sørensen nor Knudsen definitions of salinity correspond to the total dissolved solids in a sample of sea water. The latter quantity can be obtained only by summing the results of analyses for each of the dissolved constituents.

In the literature of oceanography the term salinity appears to have been used to indicate each of the three properties mentioned above, that is, (a) the quantity of dissolved solids, (b) the property defined by Sørensen, and (c) the property defined by equation (1). Superficially, they are the same. Basically they are different, and their use interchangeably or without clearly indicating which property is meant leads to misunderstanding. Strictly speaking, salinity as defined by equation (1) is the only valid use of the term for all of the data now in existence, except the nine direct measurements made according to the Sørensen definition.

The main source of confusion appears to be in the interpretation given to equation (1) and to properties of definitions and functional relationships. Equation (1) can be considered to be either (a) the definition of S‰ or (b) an empirical relationship between two sea water properties S‰ and Cl‰ each of which must be defined other than by the relationship. It cannot be both, although the two meanings coincide under the special conditions of constant ionic ratios. There are fundamentally two different points of view, each with its own limitations and attributes.

If equation (1) is used as the definition of salinity, the notions of error, precision and accuracy of salinity have no meaning. So defined, S‰ need not even be a property of real sea water. It is merely a number established by the indicated arithmetical operations. Essentially what is done here is to say that we will define the property S‰ in terms of Cl‰ (otherwise defined) by the general expression:

$$S‰ = a + b\,Cl‰ \tag{2}$$

where the choice of values for a and b are without limit. All that is needed is agreement, among those using the relationship, on the values to be given to a and b. In practice they are chosen such that computed values of S‰ correspond as closely as possible with a property obtained under some other definition - the Sørensen definition.

On the other hand, if equation (1) is taken as an empirical relationship between two otherwise defined properties, error, precision and accuracy now have meaning. Taken from this point of view, the uncertainty in predicting S‰ (Sørensen definition) from measured values of chlorinity may be as large as 0.04 ‰, a figure obtained by statistical analysis of the nine pairs of measurements which produced equation (1). Considering the limited geographic distribution of the nine samples analyzed, the uncertainty, when applied to all ocean waters, may be larger.

It must be realized that if sea water composition is to be indicated by a single parameter, applicable to the whole ocean, we must be prepared to accept a degree of uncertainty in the relationships between various sea water properties that are affected by variations in the ionic ratios that occur from place to place in the oceans.

Since the measurements by Cox et al strongly suggest that ionic ratios in sea water vary from one location to another, the panel felt it desirable to redefine salinity in such a way as to clarify its meaning and to make it consistent with the new information.

The recommended definition of salinity was arrived at by the following procedure. If it is assumed tacitly that salinity is closely related to density of sea water, a definition can be established for salinity in terms of the density of sea water at 0°C. (Density being designated by the density anomaly $\sigma_o = 10^3(\sigma_o - 1)$, where σ_o is density in grams per cubic centimetre at 0°C.) Such a definition would require that salinity be a unique function of σ_o, of the form :

$$S = S(\sigma_o) \text{ or } \sigma_o = \sigma_o(S). \tag{3}$$

This definition is incomplete because the salinity can be any function of σ_o. It is therefore possible to select further requirements for salinity to satisfy. The most important additional property is that salinity be conservative. Hence, for salinity and chlorinity to be conserved simultaneously, the relationship between the two must be of the form

$$S = aCl \tag{4}$$

where "a" is a constant. Equation (4) is interpreted to mean that for a given sample of sea water, the salinity is proportional to chlorinity and the proportionality factor is not affected by the addition or removal of pure water.

The relationship given in (4) differs from Knudsen's relationship (1) by the absence of a constant. The constant was introduced into Knudsen's formula to compensate for the fact that chlorinity is a poor estimate of salinity for waters that are highly diluted by land drainage which tend to be low in chlorides but high in other salts. Salinity, defined by Knudsen's formula, is not conservative for addition or removal of pure water. Over most of the oceans, the principal exchange of water occurs by evaporation and precipitation. These processes can be considered to a first approximation as consisting of the addition and removal of pure water.

Strictly speaking, the coefficient "a" in (4) will vary for individual water masses because (3) and (4) cannot be satisfied simultaneously except for constant ionic ratios. Hence, if we demand that (3) be a unique function, we must relax (4) to make the coefficient a constant. For "a" to be a constant, the coefficient must correspond to the average ratio of salinity to chlorinity, i.e.

$$a = S/Cl \tag{5}$$

As the value of "a" is arbitrary, we are free to choose it so that the salinity corresponds closely to salinity determined under the previous definition. The correspondence cannot be exact at all salinities. By specifying exact correspondence at a salinity of 35‰, we obtain :

$$S = aCl = 0.03 + 1.805\ Cl = 35‰ \tag{6}$$

Hence,

$$a = 1.805 \times 35/34.97 = 1.8065_5 \tag{7}$$

Thus, salinity S, as determined by chloride titration, will differ from that obtained from Knudsen's formula S' by

$$S = S' - S = 0.03 + 1.805\ Cl - 1.8065_5\ Cl = 0.03\ (1 - S/35) \tag{8}$$

The differences for various salinities are :

S	ΔS
0‰	+ 0.03‰
10	+ 0.021
20	+ 0.013
30	+ 0.004
35	0.000
40	- 0.004

In the normal open ocean range of salinities (30-40‰), the differences between the two definitions cannot be distinguished from zero except for the most accurate weight titration determinations of chlorinity. Lower salinities (<30‰) are encountered only in coastal regions and partially enclosed seas in which greater variation of sea water composition can be expected and where ambient variations are much larger than in the open oceans. High precision is of lesser significance. Consequently, no serious difficulties can be expected in comparing "new" salinities with "old" salinities over the entire range encountered in the oceans.

The procedure to set up the new definition of salinity is as follows : first, a representative set of sea water samples from all oceans is analyzed to determine as accurately as possible both the chlorinity and the density at 0°C, as has been by Cox et al. From these pairs of numbers, a relationship of the form

$$\sigma_0 = \sigma_0 \, (Cl) \tag{9}$$

is determined by regression analysis. By virtue of the relationship given in (4), (9) can be transformed to yield a functional relationship between σ_0 and salinity. This relationship is then adopted as the definition of salinity. Thus, for each σ_0, there will be a uniquely determined salinity. The relationship of other properties to salinity can be determined by measuring the property and σ_0, converting σ_0 to salinity and finding the regression equation for salinity in terms of the measured property. For each property measured, there will be a calculated degree of uncertainty in deriving density or any of the other properties. Thus, a measurement of conductivity may give a relatively precise estimate of density but a less precise estimate of chlorinity. Conversely, measurement of chlorinity would not provide a precise estimate of density or conductivity. The regression analysis would provide an estimate of the precision of calculating related properties from a measurement of a given property. The procedure is general and no re-definition would be required regardless of the development of new techniques for estimating salt content.

Additional measurements which are needed

The results obtained up to May 1962 (Cox et al, 1962) relate conductivity and density at 0°C, both in arbitrary units, to chlorinity. The next step is to convert these measurements to absolute units; this it is proposed to do as soon as is practicable.

The density of a selected range of samples will be determined in g/cm^3 by a method similar to that of Knudsen (Forch, Knudsen and Sørensen, 1902); a sinker slightly heavier than the water is weighted first in pure water at 4.0°C and then in the sample at 0°C. From these values it will be possible to convert all the density measurements to absolute units.

An apparatus is also under construction for the absolute determination of conductivity. In principle this will involve a quartz tube of precisely known dimensions, with the open end immersed in the test sample. The resistance is measured between a platinum electrode in the tube and another in the solution. The electrode in the tube is then moved a known distance and the resistance measured again. The difference between the two readings depends only on the dimensions of the tube, the distance the electrode is moved, and the absolute conductivity of the solution. It is hoped in this way to measure the absolute conductivity of the standard sea water to one part in 10^5, and the absolute conductivity of the remaining samples can then be calculated from the present relative measurements.

The data available will then provide for the following :

1) To compute empirical relationships between conductivity, chlorinity and σ_0.
2) To derive the new definition of salinity in terms of σ_0.
3) To compute relationships and prepare tables connecting the newly defined salinity with conductivity and chlorinity.

The measurements of refractive index have been deferred, on the advice of the National Physical Laboratory, until all the samples are available, as the adjustment of the refractometer is a long operation. It is hoped to undertake these measurements late in 1962, by which time the collection of the samples should be substantially complete. Tables will then be prepared relating refractive index to salinity.

In addition to the tables already mentioned, the new oceanographic tables should include the following information:

1) The effect of temperature on electrolytic conductivity, at various salinities.
2) The effect of pressure on electrolytic conductivity, at various salinities and temperatures.
3) The compressibility of sea water at various temperatures and salinities.
3a) Perhaps the coefficient of thermal expansion, at various salinities and pressures.
4) The velocity of sound, as a function of temperature, salinity and pressure.

(3) and (3a) are interdependent, but for convenience it may be better to present the information in both forms. If practicable it might be better to measure both variables as a cross-check.

On these variables listed above (1) is listed by Thomas, Thompson and Utterback (1934) but the values at high salinities at least are doubtful, and will be re-determined with the new absolute conductivity apparatus.

(2) was investigated by Hamon (1958) but the range and precision are inadequate. Further measurements are being made at Woods Hole and the University of Kiel.

(3) and (3a), our present tables are based on the measurements of Ekman (1908). Recent computations by Crease (private comm., shortly to be published) based on the velocity of sound, agree well with Ekman's figures. They do not agree so well with some more recent values by Kennedy (private comm.). The situation is not very satisfactory. There would seem to be a need for further measurements of either compressibility or thermal expansion, or both. The panel would like to know of any measurements in this field which are in progress or contemplated in the near future.

(4) The recent work of Wilson (1960 a, b) gives us excellent values for sound velocity. Unfortunately no measurements were made at high salinity (above 37‰) and to complete the coverage it would be desirable to add some determinations up to 40‰ at least.

Recommendations

After consideration of the various matters discussed above, the panel adopted the following recommendations:

1) That as soon as practicable Copenhagen Standard Sea Water be certified in electrolytic conductivity as well as chlorinity.
2) That Copenhagen Standard Sea Water be recognized internationally as the primary standard for both chlorinity and conductivity measurements as soon as recommendation (1) has been carried out. All laboratories

now preparing independent sub-standards are urged to compare these as a routine with the primary standard.

3) That all laboratories co-operate with the fundamental investigations being undertaken at the National Institute of Oceanography (UK) by providing, upon request, sea water samples required for these investigations.

4) That in order that the new definition of salinity be as nearly as is possible comparable with the old, the following procedure be adopted:
   a) That the relationship between salinity and chlorinity be arbitrarily established as S‰ = 1.80655 Cl‰ .
   b) That an empirical relationship be computed from the data of Cox et al. connecting chlorinity with σ_0.
   c) From (a) and (b), a relationship be established between salinity and σ_0. This relationship shall then be adopted as the definition of salinity.

5) That the empirical relationship between conductivity at 15°C and salinity defined as in (4) be established from the data of Cox et al., and this be accepted as the means for converting measured conductivity to salinities.

6) That a relationship similarly be established between refractive index, n, at a temperature to be decided, and S‰

7) That the statements of the relationships between the four measured quantities, σ_0, γ, n and Cl ‰, include an appropriate estimate of precision.

8) That the experimental determination of the temperature and pressure effects on conductivity and density be carried out as soon as possible, and that the status of all work in progress on such determinations be reported promptly to the Chairman of the Panel.

9) That when the above recommendations have been carried out, new international oceanographic tables be computed and published.

10) That in these new oceanographic tables density and specific volume functions shall be in units of mass and length (g. and cm.)

11) That when values of salinity are reported in the literature or recorded in data libraries the method of measurement (e.g. conductivity, chlorinity) by which the values were obtained shall always be indicated.

12) That instruments used for measuring electrolytic conductivity of sea water be so calibrated that their readings can be expressed in terms of absolute conductance.

13) That these recommendations be communicated to ICES, IAPO, SCOR, IOC and other interested bodies by the Office of Oceanography, Unesco.

References

Cox, R.A.; Culkin, F.; Riley, J.P. 1961. New investigations in the determination of salinity.

Cox, R.A.; Culkin, F.; Greenhalgh; Riley, J.P. 1962. The chlorinity, conductivity, and density of sea water. Nature, Vol. 193, No. 4815, p. 518-20, Feb. 10.

Knudsen, M.; Forch, C.; Sørensen, S.P.L. 1902. Bericht über die chemische und physikalische Untersuchung des Seewassers und die Aufstellung der neuen hydrographischen Tabellen. Wissen. Meeresunt.herausgeg. Kommiss. f. Untersuchung deutsch.Meere,Kiel Ab. Kiel N.F.B. 6.

Bather; Riley, J.P. 1953. Conseil Int. Exp. de la Mer J. du Conseil 18 277.

Forch, C.; Knudsen, M.; Sørensen, S.P.L. 1902. D. Kgl. Danske Videnske, Selske Skrifter, 6, Raekke, Naturvidenske og mathem. 12 1.

Carritt, D.E.; Carpenter, J.H. The composition of Sea Water and the Salinity - Chlorinity - Density Problem. In NAS-NRC Pub. 600 (1959).

Wilson, W.D. 1960 (a) The Speed of Sound in Sea Water as a function of T,P,S. J. Acoust. Soc. Amer. 32, 6, p. 641.

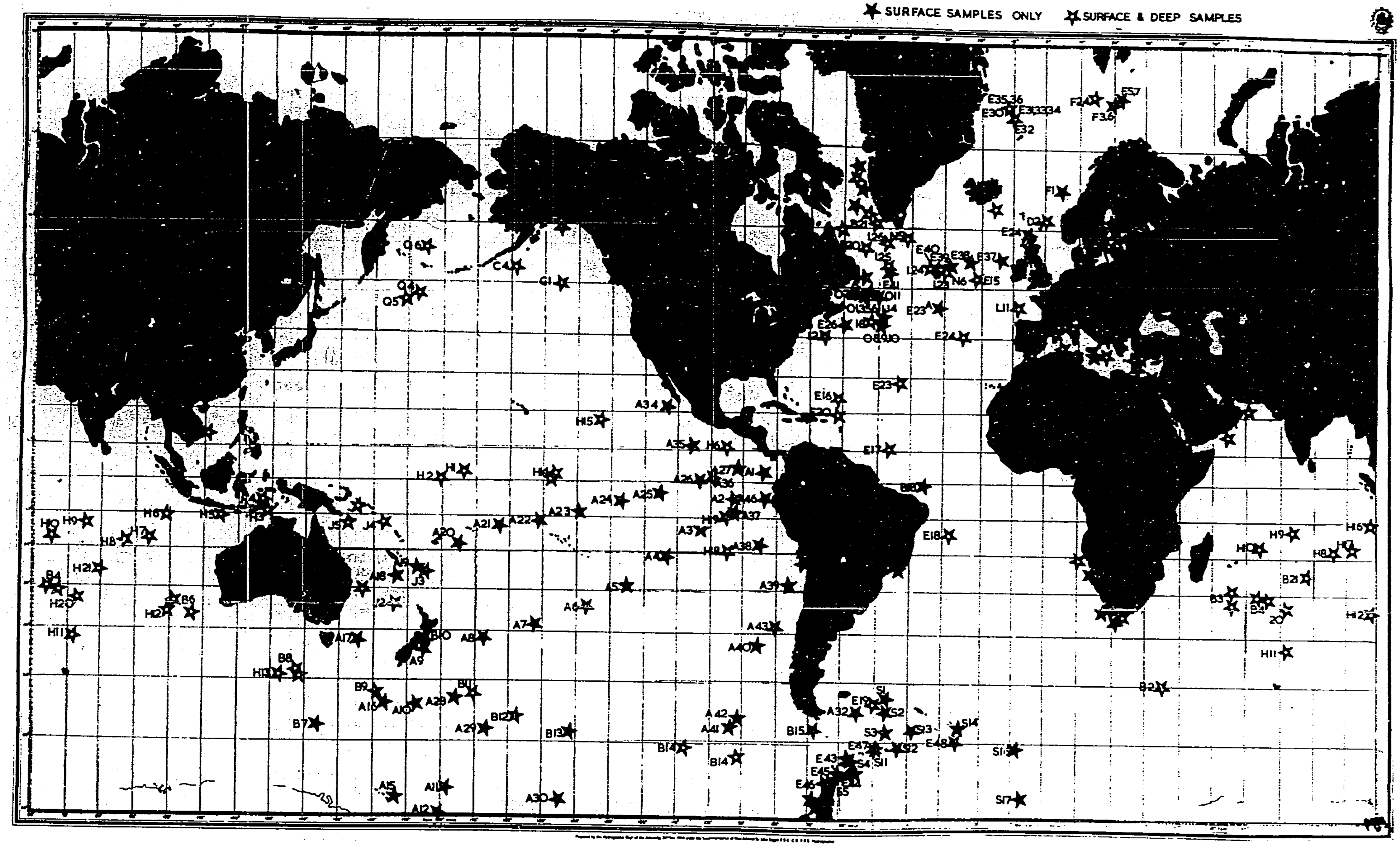
Wilson, W.D. 1960 (b). Equations for the speed of sound in sea water. J. Acoust. Soc. Amer. 32, 10, p. 1357.

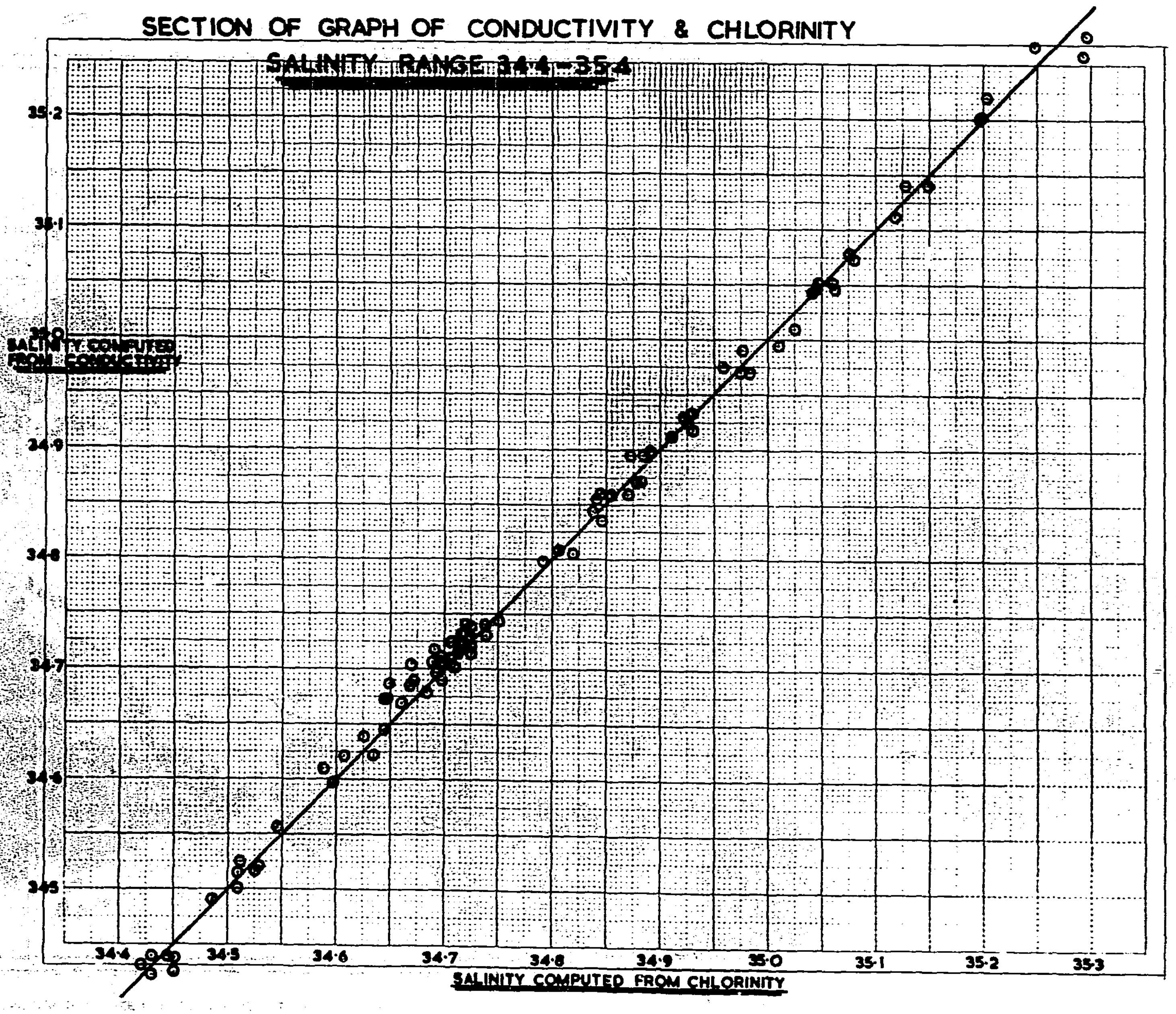
Thomas; Thompson; Utterback. 1934. The electrical conductivity of sea water. J. du Conseil, 9, 28-35.

Ekman, V.W. 1908. Die Zusammendrückbarkeit des Meerwassers. Pub. de Circonstances 43, 47 p.

Hamon, B.V. 1958. The effect of pressure on the electrical conductivity of sea water. J. Mar. Research, 16, 2 p. 83-9.

LOCATIONS FROM WHICH SAMPLES HAVE BEEN RECEIVED AT N.I.O. UP TO MAY 1962

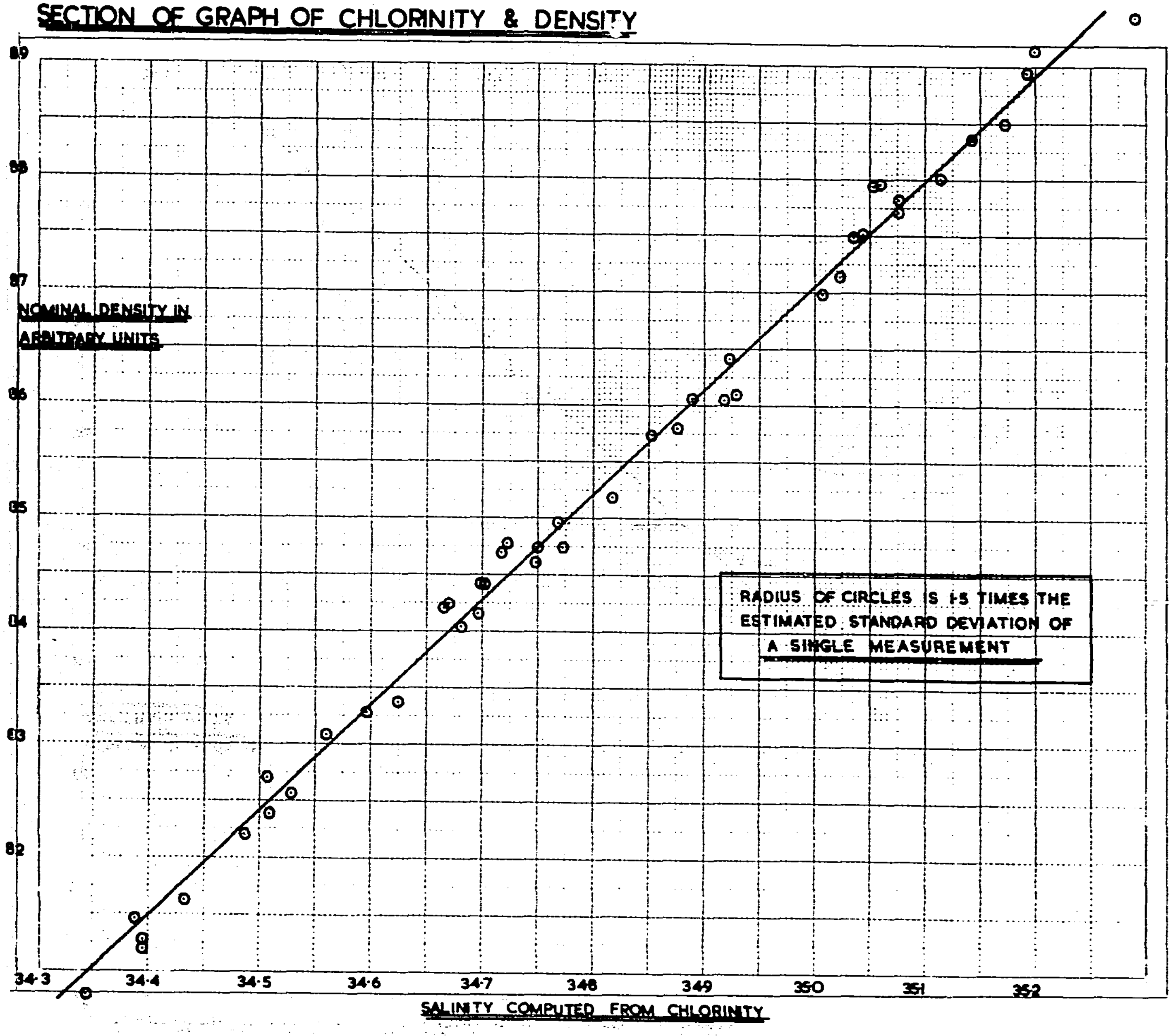




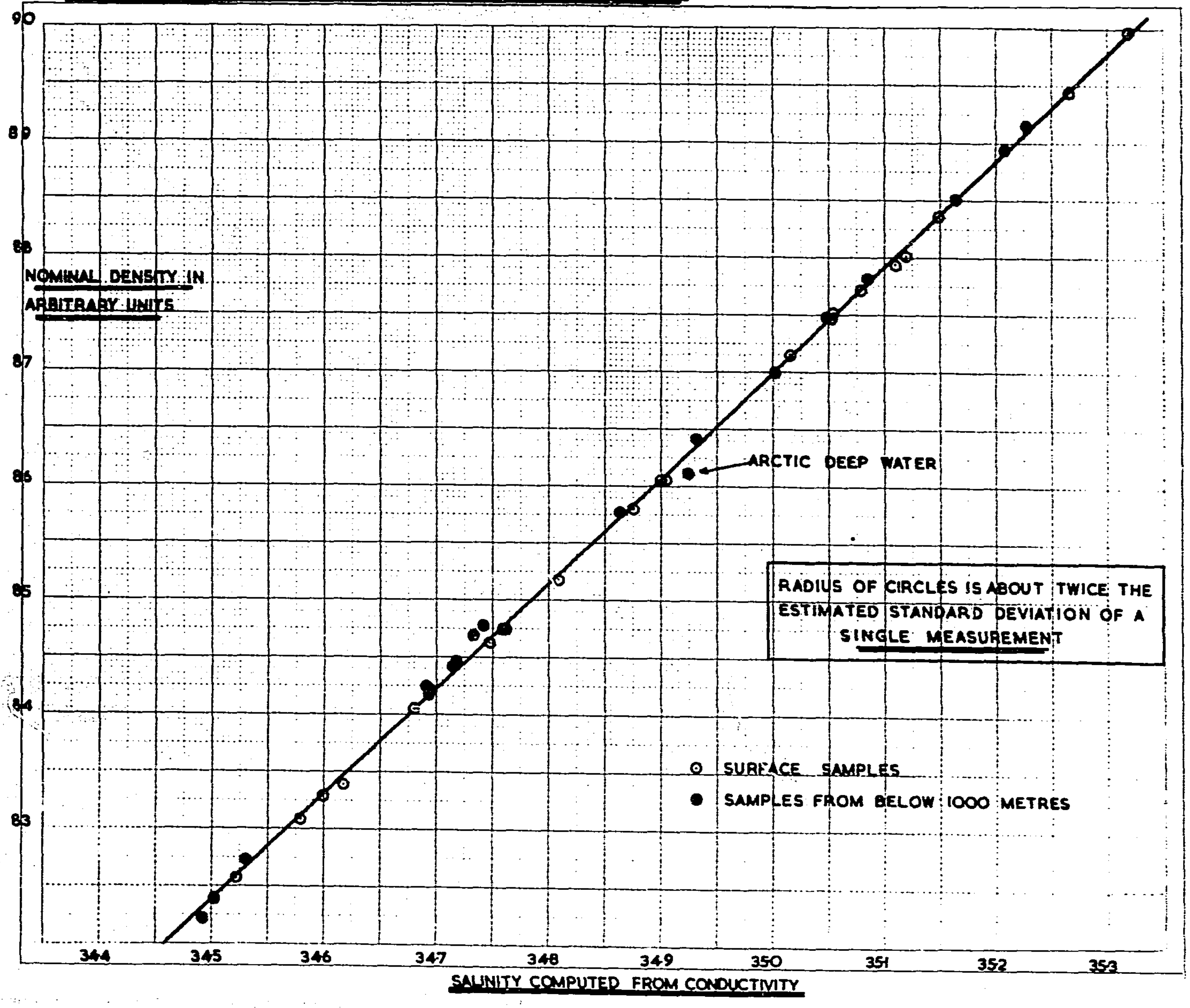
SECTION OF GRAPH OF CONDUCTIVITY & CHLORINITY

SALINITY RANGE 34·4 – 35·4

SECTION OF GRAPH OF CHLORINITY & DENSITY



SECTION OF GRAPH OF CONDUCTIVITY & DENSITY



APPENDIX II

NS/9/114B
Berkeley, California
19 Aug. 1963

UNITED NATIONS EDUCATIONAL
SCIENTIFIC AND CULTURAL ORGANIZATION

Second Report of Joint Panel on the Equation of State of Sea Water

Introduction

I. A panel, composed of representatives from IAPO, ICES, SCOR and Unesco, was organized under Unesco sponsorship, upon the recommendation of the Hydrographical Committee of ICES, in order to:

"(a) review present knowledge of the equation of state of sea water, in particular of the properties of chlorinity, salinity, density, conductivity and refractive index, and the relationship among these properties,

(b) to consider whether redefinition of any of these properties is necessary, and

(c) to advise on such further investigation as may be required"

First Panel Report

The panel met at Unesco Headquarters, Paris, on 23 to 25 May 1962. A report of the results of the meeting was circulated by Unesco under the designation NS/9/114B, dated Paris 4 December 1962. A limited number of copies of the report are available at the present meeting. Those interested in obtaining a copy contact Dr. K. N. Fedorov (Unesco).

In very brief summary, the first report of the panel noted:

(a) Cox and co-workers have collected approximately 300 samples of sea water, which have good representation of all oceans and depths. Approximately half of the samples have been analyzed for chlorinity, relative conductivity, and relative density.

(b) The relationships between chlorinity and either density or conductivity showed a larger scatter than could be inferred from previous data. For a given density or conductivity the chlorinity was found to vary by approximately 0.03‰. However, the conductivity-density relationship showed a smaller scatter. For a given density the conductivity (in chlorinity equivalence) varied by only approximately 0.004‰. That is, density can be predicted from measured value of conductivity with very nearly an order of magnitude better precision than is possible from measured value of chlorinity.

(c) The information now contained in the chlorinity-density parts of Tables, and the relationships from which the Tables were computed, is in error with respect to the precision implied by the number of significant figures tabulated. The Tables suggest a more precise relationship than actually exists in natural sea water.

(d) The results of the studies of Cox and co-workers suggest that the notion of the constancy of the relative proportions of major dissolved constituents in sea water is more limited than had been inferred from previous data.

(e) The panel made recommendations with regard to :

1) certification of Copenhagen Standard Sea Water for both chlorinity and conductivity.

2) the derivation of new empirical relations, based upon the work of Cox et al, between density and conductivity, and between density and chlorinity.

3) the redefinition of salinity.

Second Panel Meeting

The Panel met in Berkeley, California on 16 to 18 Aug. 1963 to consider the comments generated by their report of December 4, 1962, to examine new data obtained since the last meeting.

The recommendations, as restated during the present meeting of the panel, are included in this report.

Work completed since the first report.

The work completed since the first report includes some attempts at absolute density determination, and a considerable number of chemical analyses.

Taking the density measurements first, an apparatus has been built to compare the density of sea water samples with that of pure water. This consists of a large quartz bulb, ballasted to be slightly denser than sea water. This is immersed in the sample, and suspended from a sensitive balance by a fine wire of platinum iridium alloy.

The sample is held in a vacuum flask, maintained at 4°C by immersion in a thermostat.

This apparatus gives values of density reproduceable to about ± 2 parts in 10^6. However a serious difficulty has arisen which unfortunately was not foreseen. Sigma-0 of sea water is a specific gravity, a ratio of the density to that of "pure water" at 4°C. But what is pure water? This point will be discussed at greater length at the AIPO meeting, but we have found that "pure water" distilled from sea water can vary in density by at least 30 parts per million, depending on its source.

The source of these variations is almost certainly variation in isotopic ratios, of H-2 and H-1 and perhaps O-18 and O-16. We would be glad to hear of any laboratory which could accept a small number of water samples and determine these ratios fairly quickly, as otherwise there may be a considerable delay in obtaining the information.

The chemical analyses are the joint work of Dr. Riley and his staff at Liverpool, who have determined the acid radicles (anions), and Dr. Culkin at Wormley, who has been determining the metals (cations). The acid radicles sulfate, fluoride, borate, bromide and chloride have been measured in each of approximately 450 samples. The acid radicle results show extremely constant ratios to chlorinity. Of those measured, the only acid radicle which could have a bearing on the conductivity-chlorinity ratios is sulphate. Riley finds no variation in sulphate/chlorinity ratio more than ± 0.3% from the mean. The standard deviation of the measurement is about 0.15%, so these variations are hardly significant. It seems that sulphate/chloride ratio variations cannot account for more than approximately one quarter of the variation found in the conductivity/chlorinity ratio.

However the variations in metal analyses are more significant. The two metals which have so far given interesting results are calcium and magnesium. A summary of the results is in table one below.

Table 1

Calcium Analyses

Samples	Mean Ca/Cl ratio	Range	Standard deviation
Std Sea Water (12 samples)	0.02145	0.02141 0.02152	0.18%
Surface (33 samples)	0.02147	0.02132 0.02159	0.29%
Intermediate (8 samples)	0.02152	0.02145 0.02156	0.22%
Deep (16 samples)	0.02154	0.02147 0.02165	0.20%

Magnesium Analyses

Samples	Mean Mg/Cl	Range	Std. dev.
Std. Sea Water	0.06677	0.06666 0.06684	0.05%
Surface	0.06680	0.06640 0.00709	0.17%
Intermediate	0.06679	0.06666 0.06691	0.13%
Deep	0.06682	0.06668 0.06698	0.12%

These results will be discussed in greater detail at the AIPO meeting but some of the more important points are these :

1) Calcium, on average, increases with depth. If this represents solution of calcium as bicarbonate, the increase could correspond to an apparent salinity increase (from a conductivity measurement) of about 0.01‰ , about one quarter of the variations we find. There is a strong negative correlation between the calcium/chlorinity ratio and chlorinity/conductivity ratio, i.e. high calcium means high conductivity. We can see no significant regional variations in the calcium/chlorinity ratio.

2) Magnesium, on the other hand, does not show any correlation with depth. There are, however, strong regional trends. All our deep Mediterranean samples, for example, are well below average in magnesium, while surface samples from the N. Atlantic are all high. The variations in magnesium on a weight basis, are about double those of calcium. Moreover, the partial ionic conductivity of magnesium is lower than calcium, so replacement of, for example, sodium by magnesium has a greater effect than replacement by calcium. The variations found in magnesium could account for about half of the observed chlorinity/conductivity variations.

The correlation between the chemical analysis and other variations is far from perfect. This is partly because the samples for chemical analysis have been selected from the far larger number on which we have conductivity and chlorinity figures. The samples selected for chemical analysis are those which showed the largest departure from the mean chlorinity/conductivity ratio. They hence will include all the bad results, all the errors, from our 500 samples. We think that the small number of apparent "misfits" are probably errors, and that the variations in chlorinity/conductivity ratios can be satisfactorily explained on a basis of variations in chemical composition.

Restatement of the recommendations in the first report.

Most of the criticism of the first report has centered on the proposed new definition of salinity. Some of these comments have made it clear that the readers did not entirely understand the proposals, so the committee has decided it would be worthwhile to re-state this section of the report in the simplest possible terms.

The principle facts on which the decision was based to re-define salinity are these :

1) Owing to the relative concentrations of the various ions in sea water being to some extent variable, the relationships between chlorinity and density, and between chlorinity and conductivity, are also somewhat variable from place to place.

2) The relationship between conductivity and density, on the other hand, is much more nearly constant.

3) Therefore, if the object is to determine density it is better to measure conductivity than chlorinity. The conductivity can then readily and precisely be converted to density.

Based on these facts alone, it would seem better to abandon the term "salinity" and report the measurements as conductivity or density. There are, however, certain difficulties. The most fundamental point is this; in the study of water masses it is convenient to characterize a body of water by three independent variables, traditionally temperature, pressure and salinity. Salinity in its literal sense, like chlorinity, is a conservative property; that is, if we mix two bodies of sea water, or dilute sea water with fresh water, the salinity or chlorinity of the mixture can be calculated by simple proportion from the corresponding values for the components of the mixture. Under this definition "salinity" as computed from chlorinity by the Knudsen formula is not conservative.

There are two other substantial arguments in favour of retaining salinity. It is the parameter currently reported on the hydrographic data cards of all data centres. Millions of such cards exist, and it would be very expensive to change them. Secondly, it is only proper to consider the needs of workers other than physical oceanographers. To a biochemist, for example, salinity has a real significance as a concentration of salt. Subtle differences in definition are immaterial to such a worker, who does not need high precision; but while a salinity of 35‰ or 3.5% has a real significance a sigma-0 of 26 means nothing. Such workers will undoubtedly prefer that salinity be retained as the reported parameter.

The objects in redefining salinity, then, are three-fold:

1) To make it a conservative property.
2) To so relate it to conductivity and density that any one of these parameters can readily be computed from another.
3) For convenience in comparing values so calculated with older data, it is desirable that numerically the new salinity shall be as near to the old value, based on chlorinity, as the natural scatter will permit.

The committee proposes to achieve this by the following steps. First we accumulate all the available observations where both chlorinity and density have been measured on the same sample. We convert the chlorinities to salinity; however, to keep the "salinity" strictly a conservative property, we do not use the Knudsen expression $S‰ = 1.805 Cl\% + 0.03$

but instead use

$$S‰ = 1.80655 Cl‰$$

since this produces an identical result at a salinity of 35 and no errors on ocean waters comparable with the uncertainty of chlorinity measurement. We now have numerous pairs of figures for density and "salinity". From them we derive an arithmetical expression, giving salinity as a function of density, to give the best possible fit to the data. This expression shall then be used to define salinity.

By the term salinity we understand an expression of the concentration by weight of dissolved substances in sea water. Because of the difficulty in measuring this quantity, we define salinity as a function of density.

We can now readily compute empirical expressions connecting conductivity and refractive index with density, and derive expressions connecting these parameters with the newly defined salinity.

Restatement of Recommendations

1) That as soon as practicable Copenhagen Standard Sea Water be certified in electrolytic conductivity as well as chlorinity.

2) That Copenhagen Standard Sea Water be recognized internationally as the primary standard for both chlorinity and conductivity measurements as soon as recommendation (1) has been carried out. All laboratories now preparing independent substandards are urged to compare these as a routine with the primary standard.

3) That all laboratories co-operate with the fundamental investigations being undertaken at the National Institute of Oceanography (UK) by providing, upon request, sea water samples required for those investigations.

4) That the new definition of salinity shall be derived in the following manner:
    a) all available measurements of chlorinity and density be assembled.
    b) the chlorinity values be converted to "salinity" by multiplying them by 1.80655.
    c) from these figures for density and "salinity" an arithmetical expression be derived to give salinity as a function of density, fitting the measurements as nearly as possible.
    d) this expression shall then be adopted as the definition of salinity.

5) That the relationship between conductivity at 15°C and salinity defined as in (4) be established from the data of Cox et al, and this be accepted as the means for converting measured conductivity to salinities.

6) That a relationship similarly be established between refractive index, n, at a temperature to be decided, and S‰ .

7) That the statements of the relationships between the four measured quantities, sigma-0, gamma, eta, and Cl‰ , include an appropriate estimate of precision.

8) That the experimental determination of the temperature and pressure effects on conductivity and density be carried out as soon as possible, and that the status of all work in progress on such determinations be reported promptly to the Chairman of the Panel.

9) That when the above recommendations have been carried out, new international oceanographic tables be computed and published.

10) That if possible in these new oceanographic tables density and specific volume functions shall be in units of mass and length (g. and cm.)

11) That when values of salinity are reported in the literature or recorded in data libraries the method of measurement (e.g. conductivity, chlorinity) by which the values were obtained shall always be indicated.

12) That instruments used for measuring electrolytic conductivity of sea water be so calibrated that their readings can be expressed in terms of absolute conductance.

13) That these recommendations be communicated to ICES, IAPO, SCOR, IOC and other interested bodies by the Office of Oceanography, Unesco.

Information Still Needed

Before the measurements obtained by Cox and co-workers can be finally analyzed to yield functional relations between absolute values of the properties measured, the following needs to be done:

1) The measurements of sigma-0 by Cox *et al.* must be standardized. Especially needed are independant checks of the variations recently found in the density of pure water from different sources. This matter should be called to the attention of the International Bureau of Weights and Measures, not only because of the importance of absolute density to oceanography but also because of the involvement of density and the definition of the latter.

2) The absolute conductivity must be determined of the standard sea water used by Cox *et al.* Funds are needed for the construction of a precision conductivity device that will yield absolute values. Approximately $8000 are needed for the modification of existing instruments and construction of new parts. The panel feels that Unesco should be asked to contribute part of the needed funds.

3) Values for the compressibility and/or thermal expansion of sea water are needed in the construction of new oceanographic tables. The panel wishes to be advised of any measurements made of these properties or of any other physical properties of sea water.

UNESCO TECHNICAL PAPERS IN MARINE SCIENCE

Titles of numbers which are out of stock

No.		Year	SCOR WG
1	First report of the joint panel on oceanographic tables and standards held at Copenhagen, 5-6 October 1964. Sponsored by Unesco, ICES, SCOR, IAPO	1965	WG 10
2	Report of the first meeting of the joint group of experts on photosynthetic radiant energy held at Moscow, 5-9 October 1964. Sponsored by Unesco, SCOR, IAPO	1965	WG 15
3	Report on the intercalibration measurements in Copenhagen, 9-13 June 1965. Organized by ICES	1966	–
4	Second report of the joint panel on oceanographic tables and standards held in Rome, 8-9 October 1965. Sponsored by SCOR, Unesco, ICES, IAPO	1966	WG 10
5	Report of the second meeting of the joint group of experts on photosynthetic radiant energy held at Kauizawa, 15-19 August 1966. Sponsored by Unesco, SCOR, IAPO	1966	WG 15
6	Report of a meeting of the joint group of experts on radiocarbon estimation of primary production held at Copenhagen, 24-26 October 1966. Sponsored by Unesco, SCOR, ICES	1967	WG 20
7	Report of the second meeting of the Committee for the Check-List of the Fishes of the North Eastern Atlantic and of the Mediterranean, London, 20-22 April 1967 Procès-verbal de la 2e réunion du Comité pour le catalogue des poissons du Nord-est atlantique et de la Méditerranée, Londres, 20-22 avril 1967	1968	–
8	Third report of the joint panel on oceanographic tables and standards, Berne, 4-5 October 1967. Sponsored by Unesco, ICES, SCOR, IAPO	1968	WG 10
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, 8-11 April 1969)	1969	–
14	Fifth report of the joint panel on oceanographic tables and standards, Kiel, 10-12 December 1969. Sponsored by Unesco, ICES, SCOR, IAPSO	1970	WG 10