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Electrolytic Conductance of Sea Water and the Salinometer[*]
(Part 1)

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1. Introduction

The specific conductance of sea water is about a million times greater than that of pure water. Furthermore, at a given temperature, the conductance increases almost linearly with increasing salinity. Therefore, the conductance should be a simple and yet far more precise measure of salinity than the usual silver nitrate titration method.

Since 1956 there has been a rapid development of electrolytic conductivity techniques, so that today more determinations of salinity are done by conductometry than titration. For instance, at Oregon State University, all the salinity samples taken after December 31, 1961 have been analyzed conductometrically.

This review paper presents a short history of the development of the conductivity techniques, discusses the nature of the electrolytic conductance of sea water and gives a brief description and precision of the various conductometric salinometers presently used. Problems in the use of international standard sea water as conductometric standard, and biogeochemical factors affecting the conductance of sea water in the ocean are also discussed.

Historical sketch

According to THOMAS et al. (1934), KARSTEN (1897) first suggested the measurement of

electrical conductivity as a means for ascertaining the concentration of the salts in sea water. TORNÖE (1895) and KNUDSEN (1900) continued the work. However, since, presumably, the chemical technique was then superior to the conductometric technique, Knudsen's main effort was directed towards an elaborate modification of Mohr's titration. The Knudsen titration and his chlorinity-salinity-density table have been one of the basic tools of the oceanographer ever since.

RUPPIN (1907) determined the specific conductance of seven sea water samples at 0°, 15°, and 25°C. THURAS (1918) and van del POL (1918) repeated the measurements at 25°C. WEIBEL and THURAS (1918) worked on a conductivity recorder. RIVERS-MOORE (1918) showed that the conductance did not vary with frequency changes as high as 100,000 cycles.

The first shipboard conductivity salinometer was developed by WENNER et al. (1930). This meter featured a good thermostat, a number of similar glass cells in the constant temperature bath to hold samples and a standard sea water, and a medium frequency (a.c., 1,000 cycles per second) for the bridge circuit. The instrument had a precision of 0.02‰ S, which was comparable to the precision of Knudsen's titration method.

The best available conductance values for sea water are that of THOMAS et al. (1934) although POLLAK (1954) pointed out two probable sources of errors in their data. They measured the specific conductance of eight sea water samples in the chlorinity range 5.147 to 19.227‰ at 5°C intervals from 0° to 25°C inclusive. Thirteen additional determinations were made at 25°C in the chlorinity range 1.476 to 21.398‰. Their sea water samples came from the Pacific Ocean, the Gulf of Alaska, Puget Sound, the Indian

Ocean and the Mediterranean Sea from depths of 0 to 2,000 meters.

BEIN et al. (1935) measured conductance as a function of temperature and salinity. Their objective was to compare direct density measurements with values computed from various parameters including conductance. Their data are tabulated by DIETRICH (1963, p 83).

GHEORGHIU and CALINICENCO (1940) studied the temperature dependency of the sea water conductance at varying chlorinities. However, from Weyl's (1964) critical reexamination of the temperature dependency, it is clear that their data do not compare in precision with those of THOMAS et al. (1934).

A continuous salinity-temperature-depth recorder was developed by JACOBSON (1948). The instrument measures temperature over the range from 28° to 90°F and specific electrical conductance from 0.00 to 0.07 ohm^{-1} cm^{-1}, from which salinity is computed. Electrical conductance is measured with a tubular cell through which the sea water passes. The cell forms one branch of a Wheatstone bridge, and the circuit is retained in balance by an amplifier and a servomotor. The instrument has been used to a depth of about 400 m (1,200 ft.) for inshore surveys in shoal water and in ocean areas where its precision of 0.2°F and 0.3‰ S are adequate.

FORD (1949) tested applications and operating characteristics of the Jacobson's instrument in estuaries and in the Gulf Stream. Between chemical analyses and the instrumental measurements of salinities, he found systematic errors of +0.13 to −0.48‰ and an inherent error spread of +0.21 to −0.27‰. Ideally, the systematic error may be reduced to zero but the inherent error is the real uncertainty in the instrument's ability.

HAMON (1955) has published preliminary notes on a temperature-salinity-depth recorder. His instrument gives a precision of 0.1°C for temperature and 0.05‰ for salinity. It can be lowered to a depth of 1,000 meters.

COX (1955) reviewed the works on the measurement of salinity by electrical means. He covered the works of JACOBSON (1948), FORD (1949) and MILLER (1954) on Jacobson's

continuous temperature-salinity-depth recorder, of DORRESTEIN (1954) on the improvement of the continuous-recording instrument, and the radio-frequency instruments, about 10 Mc/s, of McCOURT (1953) and HARWELL (1954 ab).

SIEDLER (1963) briefly reviewed three methods of measuring conductance: (1) the electrode, (2) the capacitive, and (3) the inductive methods. The three methods differ in the manner in which the solution is coupled to the measuring circuit.

The electrode method was the most common procedure in early in situ applications (JACOBSON, 1948; DORRESTEIN, 1954; HAMON, 1955; ESTERSON and PRITCHARD, 1955, SCHIEMER and PRITCHARD, 1957 and others). The advantage of this method is that conductance is directly transformed into measurable resistance. A disadvantage is that electrodes are contaminated by sea water. The second method, capacity coupling with high frequency, eliminates the contamination of electrodes by sea water (HARWELL, 1954 ab; HUEBNER, 1959) and gives an accuracy of about 0.05‰ S, but it has been primarily a laboratory model.

The inductive method does not have metallic electrodes to be contaminated by sea water. This method has been used in the open sea for a longer period by many investigators (ESTERSON and PRITCHARD, 1955; ESTERSON, 1957; HINKELMANN, 1958; PRITCHARD, 1959; GERMAN, 1960; WILLIAMS, 1961; BROWN, 1963, and others). SIEDLER (1963) used an improved model of the Hinkelmann type instrument, and obtained excellent field data. Siedler's instrument records temperature and conductance continuously down to a depth of 2,000 meters within a short period with precisions of 0.02°C for temperature and 2×10^{-5} ohm^{-1}cm^{-1} (about 0.04‰ salinity equivalent) in specific conductance. His pressure measurements have a precision equal to about one percent of the total depth range.

Serious work on the design of precision conductivity meters (salinometers) begun around 1955 at Woods Hole Oceanographic Institution (U.S.A.), University of Washington (U.S.A.), and the National Institute of Oceanography (Britain), South Africa and Australia.

Brief descriptions of these modern salinometers are given in a later section.

The highest precision of salinity measurement is needed in the computation of the density of water columns, and the calculation of geostrophic currents. Therefore, with the improvement of salinometers, the elucidation of the conductivity-density relationship has become very important. In addition, various methods of density determination should give agreeable results, so that correlation of data among different methods becomes feasible.

In order to understand the relationships among conductivity-chlorinity-salinity-density of sea water, the International Council for the Exploration of the Sea started a program to measure concurrently the conductivity, chlorinity, and density of representative samples collected from all the oceans at surface, intermediate and deep layers. The National Institute of Oceanography, under the direction of COX, analyzed these parameters (COX *et al.*, 1962). In addition, chemical analyses and measurements of refractive index are underway for the same samples. The NIO work was assisted financially by Office of Oceanography, UNESCO.

To further consider the problems involved in the conductivity-chlorinity-salinity-density relationships of sea water, a joint panel on the equation of state of sea water was appointed by ICES (International Council for the Exploration of the Sea), SCOR (Special Committee for Oceanographic Research), IAPO (International Association of Physical Oceanography) and UNESCO. The panel members are: G. DIETRICH (Germany), E. E. CARRITT (U.S.A.), R. A. COX (U.K.), N.P. FOFONOFF (Canada), F. HERMANN (Denmark), G. N. IVANOFF-FRANTZKEVICH (U.S.S.R.), and Y. MIYAKE (Japan).

The first panel meeting was held in Paris in May 1962. The recommendations drafted by the panel were summarized by COX (1963a):

(1) Salinity should be redefined in terms of density at 0°C (σ_0); the relationship being chosen to presserve, on the average, the present relationship between salinity and chlorinity.

(2) New tables should be computed relating

salinity so defined to conductivity and refractive index.

(3) As soon as practicable, Copenhagen Standard Sea-Water should be certified in conductivity as well as chlorinity.

Cox's data comparing conductivity, chlorinity, and density for sea waters obtained from all the oceans at various depths (Figure 1) are illustrated in the First Report of Joint Panel on the Equation of State of Sea Water (UNESCO, 1962) (Figures 2, 3, 4). Figure 2 shows the conductivity-chlorinity relationship. Considerable scatter exists. Therefore, the estimation of one parameter from the other suffers substantially in its precision. For instance, for two waters of same conductivity
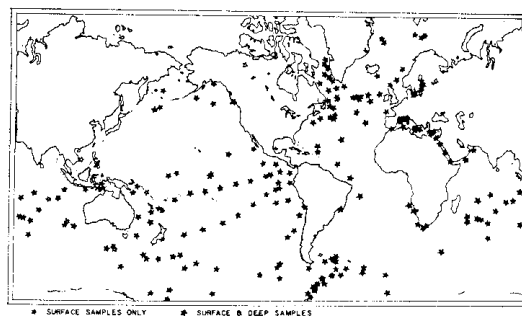

Fig. 1. Location of water sampling for the study of Conductivity-chlorinity-density relationship. (From UNESCO, 1962).
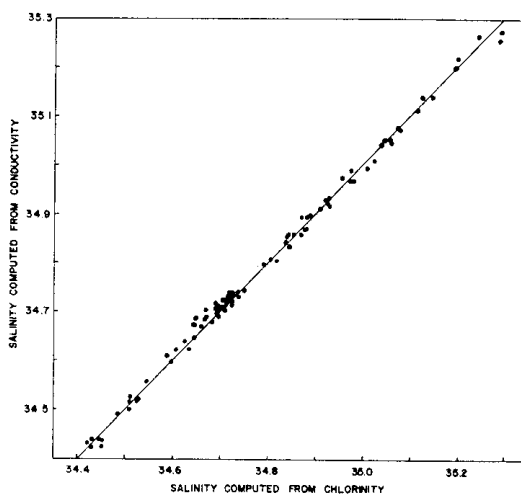

Fig. 2. Conductivity *vs.* chlorinity. (From UNESCO, 1962).

the chlorinity may vary by as much as 0.05‰.
In addition, for waters of the same chlorinity,
deep samples (below 1,000 m) tend to have a
higher relative conductivity than shallow
samples.

Figure 3 shows the chlorinity-density relation-
ship. Scatter is as great as that shown in
Figure 2. Two waters having the same density
may differ as much as 0.025 ‰ Cl.

The conductivity-density relationship (Figure
4) shows much less scatter than the two pre-
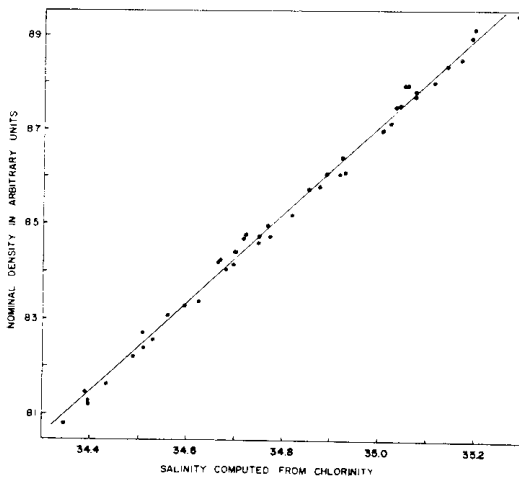vious relationships. The mean deviation from

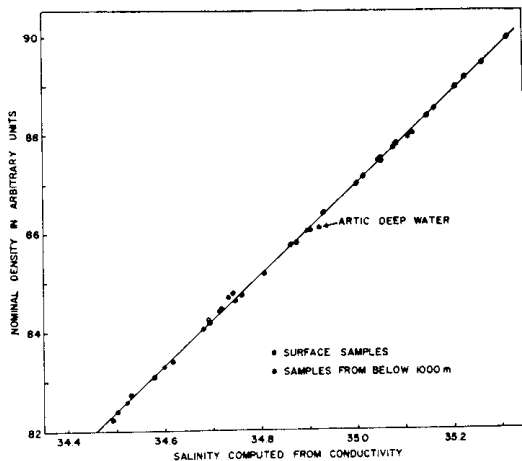Fig. 3. Chlorinity *vs.* density. (From UNESCO,
1962).

Fig. 4. Conductivity *vs.* density. (From
UNESCO, 1962).

a fitted curve is about 0.005 ‰ in equivalent
salinity. Samples showing large departure from
the curve are a few deep samples and a few
surface samples from high latitudes. For deep
waters, the contribution of heavy water on the
density cannot be ignored.

Cox's work (Figures 2, 3, 4) clearly shows
that the use of the functional relationship be-
tween chlorinity and density (σ_0) as derived
by KNUDSEN and tabulated in Knudsen's tables
for the determination of density is much less
sstisfactory than the use of the conductivity-
density relationship. Measurement of electrolytic
conductance of sea water provides a means of
predicting the density of sea water more pre-
cisely than the chlorinity method.

The second meeting of joint panel on the equa-
tion of state of sea water was held at Berkeley,
California (U.S.A.) in August, 1963. The panel
reviewed the present knowledge of the equation
of state of sea water, and in particular, of the
properties of chlorinity, salinity, density, con-
ductivity and refractive index, and the relation-
ships among them (UNESCO, 1963). The panel
considered the significance of work completed
by Cox's laboratory (NIO) since the first report
(UNESCO, 1962).

On the basis of variations in chemical com-
positon of sea water, the panel was able to
explain the variation found in the conductivity/
chlorinity ratio (Figure 2). For a variation of
0.04 ‰ salinity equivalent, the variations in
sulfate/chlorinity among samples account for
about 0.01 ‰, the dissolution of calcium car-
bonate in the deep-sea account for another
0.01 ‰, and the regional variations found in
magnesium could account for the rest of the
observed conductivity/chlorinity variations.

The panel further considered the redefinition
of salinity making a conservative property,
relating it to conductivity and density, and mak-
ing it numerically as close as possible to the
old salinity definition. Their restated recom-
mendations pertinent to the conductivity pro-
blem included in UNESCO (1963):

(1) International standard sea water should be
    certified for its conductivity and chlorinity,

(2) The relationship between the conductivity
    at 15°C and the newly defined salinity from

the data of COX et al. (1962, and also given in UNESCO, 1962) should be established,

(3) The experimental determination of temperature and pressure effects on the conductance should be made, and

(4) Salinometers should be calibrated in terms of absolute conductance.

The third panel meeting was held in Paris in October, 1964. The panel was renamed as the "Joint ICES/IAPO/SCOR/UNESCO Panel of Experts on Oceanographic Tables and Standards." They considered the work needed for publication of new oceanographic tables and the certification of standard sea water. One of the most important new tables we expect the panel to prepare is undoubtedly that of conductivity-density.

2. Electrolytic conductance of sea water

(1) General remarks

The specific conductance of sea water increases with increasing salinity, temperature and pressure. It is also a function of the nature and concentrations of the dissolved electrolytes in sea water.

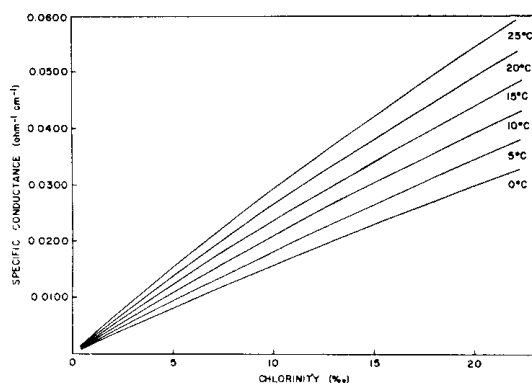Sea water is a complicated solution containing many ions, both simple and complex. Of

Fig. 5. Specific conductance of sea water at various temperatures and concentrations (From the data of THOMAS et al., 1934).

Table 1. Errors involved in the conductance data of THOMAS et al. (1934) at high salinities, at temperatures other than 25°C (from COX, personal communication).

Salinity ‰	Error ‰
35.0	0.000
35.5	0.005
36.0	0.013
36.5	0.019
37.0	0.027
37.5	0.036
38.0	0.048
38.5	0.064
39.0	0.093

these ions, Na^+, Mg^{+2}, Ca^{+2}, K^+, Cl^-, SO_4^{-2}, and HCO_3^- together make up over 99% of the electrolytes. Each of these ions contributes to the overall conductance of sea water.

The fundamental date relating the specific conductance, temperatures and the chlorinity under one atmosphere were empirically determined by THOMAS et al. (1934) (Figure 5). However, POLLAK (1954) thought that the data of THOMAS et al. were inaccurate because (1) the value for the conductance of their reference KCl solution was slightly in error, and (2) the conductance cell they used was subject to slight systematic errors. Nevertheless, reexamination of the data by COX (1963 b and personal communication) shows that, in the range of 33 to 35‰ S, the data of THOMAS et al. are correct within the precision of Cox's measurements, and serious errors appear only at higher salinities. The results of THOMAS et al. at higher salinities were lower than the true values. The extent of the error is approximately 0.013‰ at salinity 36‰ to 0.093‰ at salinity 39‰ (Table 1).

Due to the errors at high salinites, the following interpolated equations derived by THOMAS et al. are applicable at chlorinities lower than 19.3‰ (the equation for 25°C is still applicable for higher salinities):

$$0°C, \ L = 1.7875 \times 10^{-3} (Cl \ \text{‰}) - 2.9596 \times 10^{-5} (Cl \ \text{‰})^2 + 1.127 \times 10^{-6} (Cl \ \text{‰})^3 - 1.902 \times 10^{-8} (Cl \ \text{‰})^4$$

$$5°C, \ L = 2.0818 \times 10^{-3} (Cl \ \text{‰}) - 3.6859 \times 10^{-5} (Cl \ \text{‰})^2 + 1.449 \times 10^{-6} (Cl \ \text{‰})^3 - 2.520 \times 10^{-8} (Cl \ \text{‰})^4$$

$$10°C, \ L = 2.3749 \times 10^{-3} (Cl \ \text{‰}) - 4.1334 \times 10^{-5} (Cl \ \text{‰})^2 + 1.554 \times 10^{-6} (Cl \ \text{‰})^3 - 3.829 \times 10^{-8} (Cl \ \text{‰})^4$$

$$15°C, \ L = 2.7009 \times 10^{-3} (Cl \ \text{‰}) - 5.1390 \times 10^{-5} (Cl \ \text{‰})^2 + 2.097 \times 10^{-6} (Cl \ \text{‰})^3 - 3.829 \times 10^{-8} (Cl \ \text{‰})^4$$

$$20°C, \ L = 3.0191 \times 10^{-3} (Cl \ \text{‰}) - 5.6253 \times 10^{-5} (Cl \ \text{‰})^2 + 2.181 \times 10^{-6} (Cl \ \text{‰})^3 - 3.804 \times 10^{-8} (Cl \ \text{‰})^4$$

$$25°C, \quad L=3.3524 \times 10^{-3} \,(\text{Cl } \permil)-6.2481 \times 10^{-5}\,(\text{Cl } \permil)^2+2.371 \times 10^{-6}\,(\text{Cl } \permil)^3-4.049 \times 10^{-8}\,(\text{Cl } \permil)^4$$

where L denotes specific conductance of sea water in $\text{ohm}^{-1}\text{cm}^{-1}$.

For higher salinities at 15°C, COX (1963b) gives the following equation:

$$\begin{aligned}(S\ \permil)=\ &4356.6855-26{,}886.634\,(RL)\\&+68{,}955.055\,(RL)^2-93{,}754.977\,(RL)^3\\&+71{,}385.256\,(RL)^4-28{,}861.920\,(RL)^5\\&+4841.533\,(RL)^6\end{aligned}$$

where (RL) denotes the ratio of the conductivity of sea water of salinity S to that of sea water of salinity 35 ‰ at 15°C. WEYL (1964) finds that at 25°C and in the chlorinity range from 17 to 20 ‰, the following expression fits the data of THOMAS et al. with high precision:

$$\log (L)=0.892 \cdot \log (\text{Cl } \permil)+0.057625 \pm 0.00005$$

Table 2 gives the specific conductance of sea water of THOMAS et al. at various temperatures and chlorinities.

(2) Temperature dependency

The temperature coefficient of the electrical conductance of sea water varies considerably with temperature and slightly with chlorinity (Figure 6). At 0°C, the conductance of sea water increases by about 3 % per °C, while at 25°C, the increase is about 2 % per °C. At 15°C, the temperature coefficient is about 2.4 % for 1 ‰ Cl and 2.3 ‰ for 19 ‰ Cl. The chlorinity dependency of the temperature coefficient is great enough to affect the accuracy of salinometers if no compensation, or correction is made for the chlorinity dependency (COX, 1962).

WEYL (1964) critically reexamined the effect of temperature on the conductance of sea water. His comparison of the measurements of the conductance of sea water by THOMAS et al. (1934) and of NaCl solutions by BREMNER et al. (1939) shows that the temperature dependence of the two are essentially the same. He pointed out that the data of THOMAS et al. are consistent with those of GHEORGHIU and CALINICENCO (1940), but the conclusion of

Table 2. Specific conductance of sea water at various temperatures and chlorinities (from THOMAS et al. 1934). Specific conductances are in $\text{ohm}^{-1}\ \text{cm}^{-1}$.

| Cl ‰	0°C	5°C	10°C	15°C	20°C	25°C
1	.001839	.002134	.002439	.002763	.003091	.003431
2	.003556	.004125	.004714	.005338	.005971	.006628
3	.005187	.006016	.006872	.007778	.008702	.009658
4	.006758	.007845	.008985	.010133	.011337	.012583
5	.008327	.009653	.011019	.012459	.013939	.015471
6	.009878	.011444	.013063	.014758	.016512	.018324
7	.011404	.013203	.015069	.017015	.019035	.021121
8	.012905	.014934	.017042	.019235	.021514	.023868
9	.014388	.016641	.018986	.021423	.023957	.026573
10	.015852	.018329	.020906	.023584	.026367	.029242
11	.017304	.020000	.022804	.025722	.028749	.031879
12	.018741	.021655	.024684	.027841	.031109	.034489
13	.020167	.023297	.026548	.029940	.033447	.037075
14	.021585	.024929	.028397	.032024	.035765	.039638
15	.022993	.026548	.030231	.034090	.038065	.042180
16	.024393	.028156	.032050	.036138	.040345	.044701
17	.025783	.029753	.033855	.038168	.042606	.047201
18	.027162	.031336	.035644	.040176	.044844	.049677
19	.028530	.032903	.037415	.042158	.047058	.052127
20	——	——	——	——	——	.054551
21	——	——	——	——	——	.056949
22	——	——	——	——	——	.059321
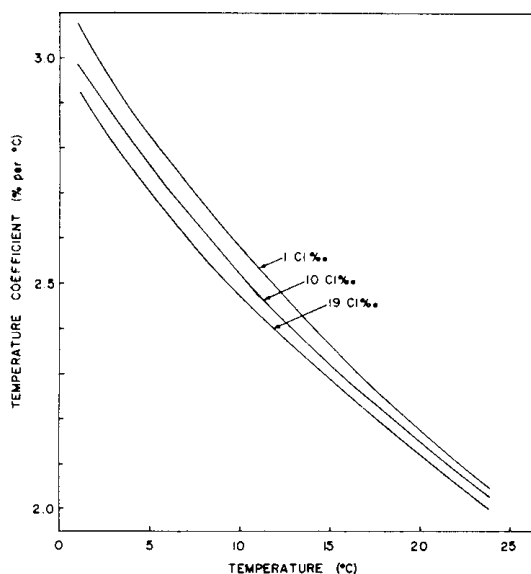
Fig. 6. Temperature coefficient of the electrical conductance of sea water as a function of temperature and chlorinity. (Plotted from the data of THOMAS et al., 1934).

GHEORGHIU and CALINICENCO that the temperature coefficient of the conductance of sea water is measurably greater than that of NaCl solutions is in error.

WEYL (1964) derived a single empirical equation to express specific conductance in the chlorinity range 17‰ to 20‰ and the temperature range from 0° to 25°C. When $T = 25 - t$ (°C), then

$$\log(L) = 0.57627 + 0.892 \log(\text{Cl } ‰)$$
$$-10^{-4}T \ [88.3 + 0.55\ T + 0.0107\ T^2$$
$$-(\text{Cl } ‰)(0.145 - 0.002\ T + 0.0002\ T^2)].$$

Conductances calculated by the above equation differ from the measured data of THOMAS et al. (1934) by less than 0.1%.

(3) Pressure dependency

There exists no sufficient data, as far as the authors are aware, on the effect of pressure on the electrical conductance of sea water. Earlier work was done by HAMON (1958) HORNE and FRYSINGER (1963). Albin BRADSHAW and K.E. SCHLEICHER (personal communication) of Woods Hole Oceanographic Institution are preparing a manuscript on this subject. Un-

published tentative results of BRADSHAW and SCHLEICHER were used by SIEDLER (1963) to evalute in situ salinometer measurements, and by BROWN (1963) to design an in situ salinity sensing system.
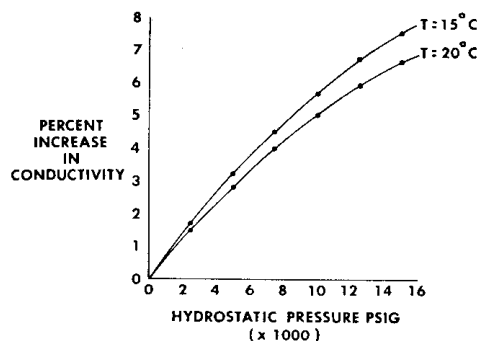

Fig. 7. Change of conductivity of sea water with pressure. (From unpublished of BRADSHAW and SCHLEICHER).

The effect of hydrostatic pressure on the conductance of sea water is considerable as shown in Figure 7 (unpublished data of BRADSHAW and SCHLEICHER, cited by BROWN, 1963). Also, the pressure effect is quite dependent on temperature as shown in Figure 8 (HAMON, 1958). The effect of pressure at 0°C is twice as great as at 30°C. Consequently, any pressure compensation must take the temperature into account.

HAMON (1958) measured the pressure coefficient of the conductance of sea water (19.7‰ Cl) at various temperatures. The coefficients vary from 1.50×10^{-5} decibar^{-1} at 0.5°C to 0.82
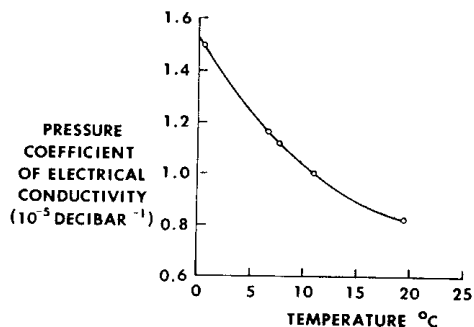

Fig. 8 Effect of temperature on pressure coefficient of electrical conductivity at 1,500 P.S.I.G. (From HAMON, 1958).

$\times 10^{-5}$ decibar^{-1} at 19.5°C (Figure 8).

HORNE and FRYSINGER (1963) measured the conductance of three sea water samples, 9.68, 17.61 and 19.376‰ Cl, at 0°, 5°, 15°, and 25°C over the pressure range 1 to 1,380 bars. They proposed the following empirical equation to express the conductance in the temperature range of 0° to 25°C and chlorinity range of 9.68‰ to 19.38‰ over the pressure range of 1 to 689 bars:

$$L_p = L_1 + (0.35 \pm 0.25)$$
$$+ (0.18 \pm 0.028) \ (Cl \ \text{‰}) \times 10^{-6} p$$

where L_p and L_1 are the specific conductance of sea water at pressures p and 1 bars respectively, and p the hydrostatic pressure in bars. Due to the uncertainty expressed within, the above equation is useful only for a first approximation of the conductance under high pressure.

As pressure is applied, sea water is compressed. Therefore, the concentration of charge-carrying species per unit volume will increase. In addition the ionization of weak electrolytes increases with increasing pressure (cited from HORNE and FRYSINGER, 1963). These facts may account for the increase in conductance with increasing pressure. Further experimental verification is needed, however, to explain the pressure effect on conductance.

(4) Electrolytes in sea water

Practically no data exist on the relationship between conductance and the kinds and concentrations of the electrolytes present in sea water. As a first approximation PARK (1964b) measured the effect of 16 electrolytes on the conductance of sea water. The effect was measured by comparing the specific conductance before and after the addition of one of the electrolytes to sea water, 35‰ S, at 23°C.

Apparent inceases in salinity due to the addition of one gram of various reagents to one kilogram of 35.00‰ S sea water at 23°C as determined by an inductive salinometer, Hytech Model 621, are given in Table 3. The results from 35.22‰ for KH$_2$PO$_4$ to 36.06 for KCl, except for HCl and NaOH. The additions of KCl, NaCl, MgCl$_2$ and CaCl$_2$ gave results near

Table 3. Apparent increase in salinity due to the addition of one gram of various reagents to one kilogram of 35.00‰ S sea water at 23°C as determined by the inductive salinometer. Hytech Model 621 (from PARK and BURT, 1963).

Reagent	Salinity (‰)	Difference of Salinity from 35.96‰
KCl	36.06	0.10
NaCl	36.04	0.08
MgCl$_2$	36.02	0.06
CaCl$_2$	35.96	0.00
KBr	35.69	−0.27
SrCl$_2$	35.68	−0.28
K$_2$SO$_4$	35.61	−0.35
Na$_2$SO$_4$	35.50	−0.46
KHCO$_3$	35.49	−0.47
K$_2$CO$_3$	35.48	−0.48
NaHCO$_3$	35.38	−0.58
MgSO$_4$	35.37	−0.59
Na$_2$CO$_3$	35.32	−0.64
KH$_2$PO$_4$	35.28	−0.68
NaOH	35.22	−0.74
HCl	40.8	4.8

the correct value of 35.96‰.

PARK (1964b) assumed that the conductance of sea water could be expressed as the sum of the conductances of the ions, or electrolytes, in sea water. For each liter of sea water,

$$1000 L = \sum_i C_i^+ \bar{A}_i^+ + \sum_i C_i^- \bar{A}_i^- = \sum_i C_i \bar{A}_i$$

where C are concentrations in equivalant/liter and A^+, A^- and $\bar{A}$ are the partial equivalent conductances of cation, anion, and electrolyte respectively. The partial equivalent conductance at a given volume, temperature, and pressure was defined by PARK as:

$$\bar{A}_i = 1000 \frac{\partial L}{\partial C_i} \Big|_{V, T, P.}$$

where V denotes volume, T, temperature and P, pressure.

With this assumption and definition, PARK (1964b) estimated the partial equivalent conductances of electrolytes in sea water. He measured the change in the specific conductance of the sea water samples before and after the addition of a small amount of an electrolyte.
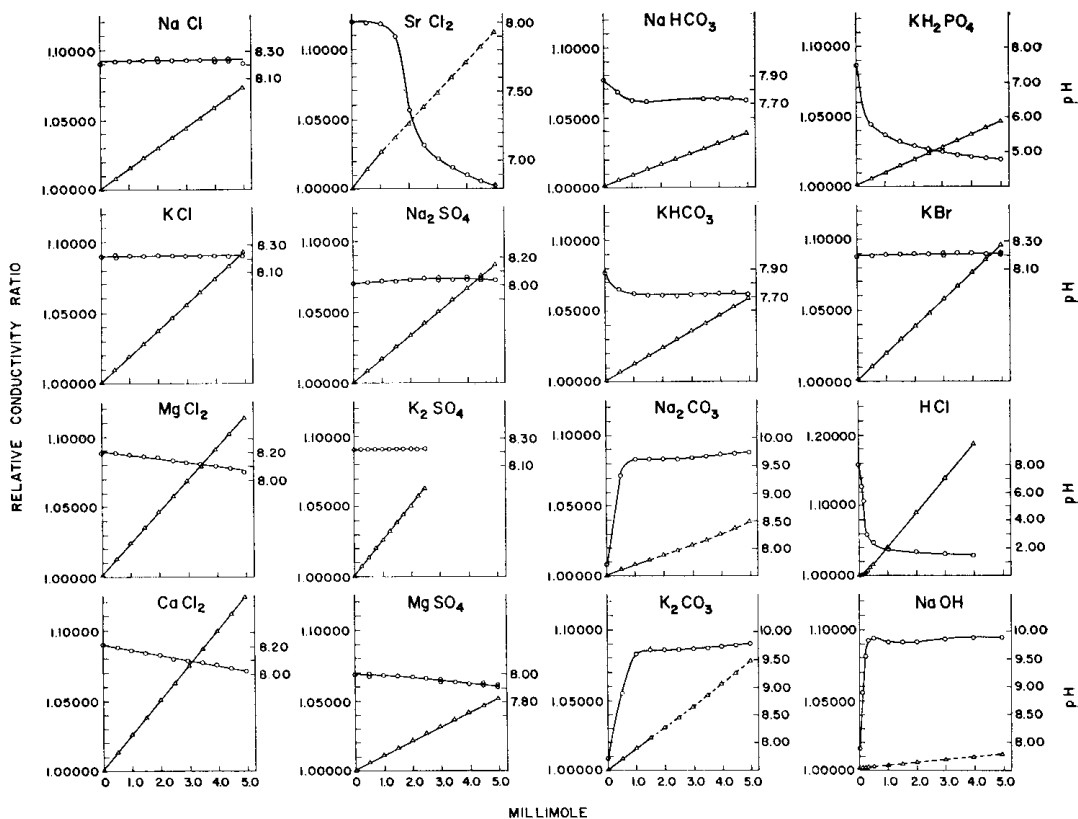
Fig. 9. Changes in relative conductivity ratio and pH $vs.$ millimoles of reagents added to 100.00 ml sea water, 36.75‰, at 23°C. (Final vol. 105.00 ml). (From PARK, 1964b).

His calculation was based on the slope of the conductance increase (Figure 9) and on calibration of the inductive salinometer (relative conductivity ratio $vs.$ salt content per liter of sea water, not $vs.$ salinity). His results are listed in Table 4.

Recently, Peter K. WEYL of Oregon State University measured the partial equivalent conductances of electrolytes in sea water 25°C. His unpublished data indicate that Park's data are about 10% too high. He further showed that it is impossible to estimate the conductive contribution of dissolved ions to the overall conductance of sea water. He defined partial equivalent conductance of salt as follows:

$$\bar{\Lambda} \equiv \Lambda^+ + \Lambda^- + \sum_i C_i \left(\frac{\partial \Lambda_i}{\partial C^+} + \frac{\partial \Lambda_i}{\partial C^-} \right)$$

where Λ^+ and Λ^- are the ionic conductance of the cationic and anionic constituents of the salt, respectively, and $\frac{\partial \Lambda_i}{\partial C^+}$ and $\frac{\partial \Lambda_i}{\partial C^-}$ denote the effect of added cation or anion on the conductance of various components in sea water. Since it is not possible to measure $\sum_i C_i \left(\frac{\partial \Lambda_i}{\partial C^+} + \frac{\partial \Lambda_i}{\partial C^-} \right)$ at present, WEYL states that the measured conductance of salt cannot be resolved into ionic constituents.

However, Park's data satisfy his assumed additivity of the conductance of electrolytes in the estimation of the over conductance of sea water:

$$1000 L = \sum_i C_i \bar{\Lambda}_i$$
$$= C_{(NaCl)} \bar{\Lambda}_{(NaCl)} + C_{(MgCl_2)} \bar{\Lambda}_{(MgCl_2)}$$
$$+ C_{(Na_2SO_4)} \bar{\Lambda}_{(Na_2SO_4)} + C_{(CaCl_2)} \bar{\Lambda}_{(CaCl_2)}$$
$$+ C_{(KCl)} \bar{\Lambda}_{(KCl)} + C_{(NaHCO_3)} \bar{\Lambda}_{(NaHCO_3)}$$

Table 4. Partial equivalent conductance of electrolytes in sea water and limiting equivalent conductance of electrolytes in aqueous solutions (ohm^{-1} cm^2) (from PARK, 1964).

Electrolyte	$\bar{\Lambda}^*$	Λ_0^{**}	$\bar{\Lambda}/\Lambda_0^{***}$
NaCl	90	126.45	0.71
KCl	116	149.86	0.77
KBr	120	151.9	0.79
$^1/_2$ MgCl$_2$	72	129.40	0.56
$^1/_2$ CaCl$_2$	78	135.84	0.57
$^1/_2$ SrCl$_2$	80	135.80	0.59
$^1/_2$ Na$_2$SO$_4$	52	129.9	0.40
$^1/_2$ K$_2$SO$_4$	78	153.5	0.51
$^1/_2$ MgSO$_4$	34	133.1	0.26
NaHCO$_3$	47	94.6	0.49
KHCO$_3$	73	118.00	0.62
$^1/_2$ Na$_2$CO$_3$	23		
$^1/_2$ K$_2$CO$_3$	49		
KH$_2$PO$_4$	57		
HCl	310	426.16	0.73
NaOH		247.8	

* Partial equivalent conductance in sea water at 35.00‰ and at 23°C.
** Limiting equivalent conductance of electrolytes in aqueous solution at 25°C. (From HARNED and OWEN, 1958. p 231 and p 697).
*** The 2°C increase in temperature, from 23°C to 25°C, corresponds to approx. 4% increase in the conductance. The ratios given here are not corrected from the temperature change.

$$+ C_{(KBr)}\bar{\lambda}_{(KBr)} + C_{(SrCl_2)}\bar{\lambda}_{(SrCl_2)}$$
$$= 51.4 \text{ ohm}^{-1}\text{cm}^2$$

The concentrations of the salts in equivalents per liter of sea water, 35.00‰ S, were based on the table for artificial sea water compiled by LYMAN and FLEMING (1940). The value of 51.4 ohm^{-1}cm^2 computed from the above relationship differs by about 1% from the original value of 50.96 ohm^{-1}cm^2 for $1000 L$ (THOMAS et al. 1934). The apparent percentage contribution of various electrolytes and ions in sea water to its overall electrical conductance at 23°C are given in Tables 5 and 6 (PARK, 1964b). For the construction of Table 6, PARK (1964b) assumed that the cation transference number of KCl in sea water is 0.49.

It should be added here that changes in the conductance while sea water is titrated with HCl (Figure 9) was utilized by PARK et al.

Table 5. Percentage contribution of various electrolytes in sea water to its overall electrical conductance 23°C (from PARK, 1964b).

Electrolyte	Equivalent/liter*	Weight (%)	Conductivity (%)
NaCl	0.4192	68.08	73
MgCl$_2$	0.1092	14.45	15
Na$_2$SO$_4$	0.0576	11.36	5.8
CaCl$_2$	0.0207	3.20	3.1
KCl	0.0093	1.93	2.1
NaHCO$_3$	0.0024	0.557	0.21
KBr	0.00084	0.278	0.19
H$_3$BO$_3$	0.00044**	0.075	
SrCl$_2$	0.00032	0.070	0.05
NaF	0.00007	0.009	

* Calculated from the data of LYMAN and FLEMING (1940). Neglected on the calculation of the conductivity per cent.
** Considered H$_3$BO$_3 \rightleftarrows$H$^+$+H$_2$BO$^-_3$ only.

Table 6. Percentage contribution of major ions in sea water to its overall electrical conductance at 35‰ and 23°C (from PARK, 1964b).

Ion	Equivalent/liter*	Weight (%)	Conductance (%)
Na$^+$	0.483	30.7	29
Mg^{+2}	0.109	3.7	2.7
Ca^{+2}	0.021	1.2	0.77
K$^+$	0.010	1.1	1.1
Sr^{+2}	0.0001	0.0	0.004
Cl$^-$	0.558	55.2	64
SO$_4^{-2}$	0.057	7.7	2.3
HCO$_3^-$	0.002	0.1	0.06
Br$^-$	0.001	0.2	0.12

* From HARVEY (1960, p 4).

(1963) to develop a conductometric method of alkalinity determination.

In summary, we emphasize that very little is understood about the fundamental electrochemical properties of ions dissolved in sea water. Each dissolved ion contributes to the conductance of sea water, but much more work is needed to ascertain each ionic role in the conductance of sea water.

3. Salinometers

Three types of salinometers have been

developed: the electrode, the inductive and the capacitive salinometers (See Introduction). At present, the electrode and the inductive salinometers are the most frequently used by oceanographers.

Since Roland A. COX of the National Institute of Oceanography (England) is summarizing the details and performances of various salinometers for publication elsewhere, we limit our discussion to the listing of the main features of the salinometers.

(1) Electrode-type salinometer

COX (1963 b) gives a brief and concise account of the development of the electrode-type salinometer. We excerpt mainly from his article.

The prototype of this instrument is that of WENNER, et al. (1930). By making fundamental changes in the use of an electronic oscillator and amplifier, SCHLEICHER and BRADSHAW (1956) of Woods Hole Oceanographic Institution developed a precise salinometer. The earlier model used a 25°C constant temperature bath with seven glass cells having a typical resistance of about 1,000 ohms. The bridge was a conventional slide-wire a.c. Wheatstone bridge, with Wagner earth circuit, driven by a 1,000 c/s oscillator. The later model used a 15°C thermostat (in order to avoid the "bubble effect" on the surface of electrode) and a self-balancing bridge with recorder.

The University of Washington salinometer (PAQUETTE, 1958 and 1959 ab) used a 15°C constant temperature bath. The earlier instrument had 6 cells, with a resistance of about 100 ohms, but the later models had up to 11 cells with a resistance of about 1,000 ohms. COX (1963 b) notes that the shortcoming of this salinometer is that each cell has a different cell constant.

The British National Institute of Oceanography salinometer (COX, 1958) has a constant temperature bath of 15°C, and 8 cells with a resistance of 3,500 ohms. The bridge power supply is a 1,700 c/s oscillator. A transformer ratio-arm bridge achieves the balance by switching-in turns on a transformer. All the cells are adjusted to have equal cell constants.

The South African instrument (ANDERSON,

et al., 1957) uses only one cell with four electrodes. An alternating current is passed through the outer electrodes, and the voltage drop across the inner electrodes is measured.

The Woods Hole instruments are currently used Woods Hole Oceanographic Institution, while the University of Washington instruments are used by Texas A & M University, University of Miami, Pacific Oceanographic Group (Canada), and University of Washington. The British type (National Institute of Oceanography) is currently used by Bedford Institute of Oceanography (Canada) and the National Institute of Oceanography (Britain).

(2) Inductive salinometer

The unique feature of this instrument is the absence of electrodes and the constant temperature bath (BROWN and HAMON, 1961). The reference resistor is a thermistor immersed in the sample, chosen and adjusted with metal resistors so that it has a similar temperature coefficient to sea water over a limited temperature range and limited oceanic salinity range (HAMON, 1956). The current is induced in the sea water by making the water form a conducting loop in a transformer bridge.

This instrument is commercially sold in Australia, U.S.A. (Hytech) and Japan (Tsurumi). It is widely used by various oceanographic laboratories in U.S.A. (Texas A & M, University of Miami, Oregon State University, Scripps Institute of Oceanography, U.S. Naval Oceanographic Office, U.S. Coast Guard, University of Alaska, Coast and Geodetic Survey, etc.); and in Australia and Japan.

(3) Capacitive salinometer

Developmental work on the radio frequency salinometer was carried out at Texas A & M University by HARWELL (1954 ab) and HUEBNER (1959). This instrument has not been perfected for field uses.

The instrument has no metallic contact with sea water. Its bridge is operated at 10 megacycles. Coupling to sea water is made through coated glass walls of the cell which act as capacitive coupling elements.

(4) *In situ* **salinometer**

The most attractive feature of the *in situ* instrument is its capacity to monitor the desired parameter continuously from the surface to depth. It also eliminates water sampling.

However, in order to have reliable instruments, study of the temperature and pressure effects on the conductivity of sea water and on the sensing device is necessary. The results of such studies should then be used in the development of a sensing device which will compensate for their effects. At present these effects have not been studied thoroughly enough.

Nevertheless, various *in situ* salinity sensing devices have been proposed (AAGAARD and VANHAAGEN, 1965; BROWN, 1963; and SKINNER, 1963) and tested (SIEDLER, 1963). In order to eliminate the problems of electrode polarization and contamination, inductively-coupled conductivity sensors with a network of temperature and pressure sensors have been preferred. BROWN (1963) gives a detailed account of his research on the temperature and pressure compensations for his proposed inductive sensing device.