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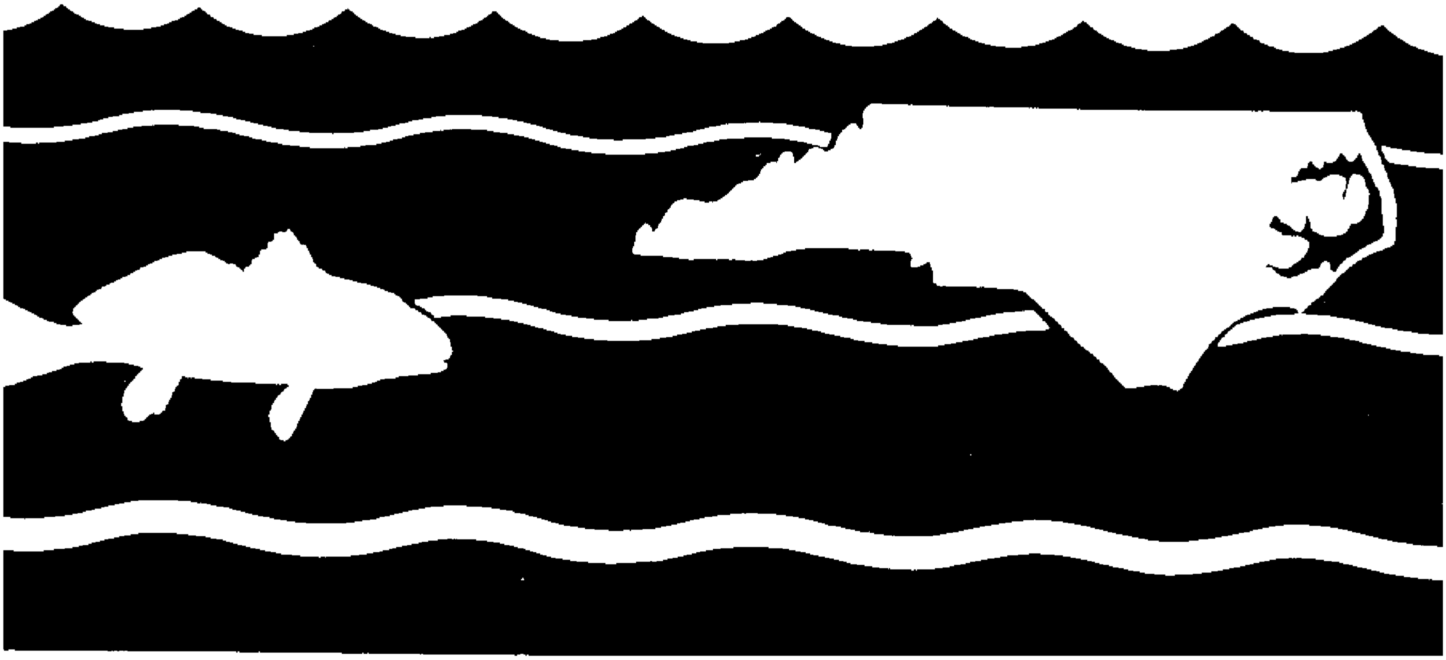

CTD SENSORS, SPECIFIC CONDUCTANCE AND THE DETERMINATION OF SALINITY

by

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Abstract

To convert the specific conductance C(S, t, p) measured by an *in situ* CTD sensor to salinity in a manner consistent with the international standard reexpression proposed by Cox et al, it is necessary to have established a means of estimating the specific conductance of seawater having a salinity of $35^{\circ}/oo$, C(35, t, 0). Third order polynomial expressions for one Red Sea Water and two Normal Water samples, each having a salinity of $35^{\circ}/oo$, are formulated and discussed. From the results of this study, it is recommended that an international expression for C(35, t, 0) be established, and in the interim, one of the expressions formulated by this study be used.

Introduction

The determination of the salinity S of seawater has traditionally been done by Knudsen titration (Forch, Knudsen and Sorensen, 1902) and expressed in terms of chlorinity Cl, i.e.,

$$S^{\circ}/oo = 0.030 + 1.8050\ Cl^{\circ}/oo. \qquad (1)$$

Seawater is a good conductor of electricity and this conductivity, strongly affected by the ionic composition and temperature of the seawater itself, has in recent years been proposed as a means of determining salinity. As a result, extensive investigations of the relationship between conductivity, chlorinity and temperature, using a large number of seawater samples from all parts of the world ocean have been undertaken by Cox et al (1967) and Brown and Allentoft (1966).

In their study, Cox et al (1967) used a salinity-chlorinity relationship slightly different from (1),

$$S^{o}/oo = 1.80655\ Cl^{o}/oo. \qquad (2)$$

As Lyman (1969) points out, either (1) or (2) will give the same value of salinity at $35^{o}/oo$ and differs by only $0.0026^{o}/oo$ at $32^{o}/oo$ or $38^{o}/oo$. The salinity-chlorinity relationship was, by international agreement in 1967, redefined as (2) to avoid the difficulty of the $0.03^{o}/oo$ salinity residue when Cl = 0.

From these investigations, Cox et al (1967) established and Wooster, Lee and Dietrich (1969) have recommended an international standard redefinition of salinity in terms of R_t (see next section), defined as the ratio of the specific conductance C(S, t, 0) of a seawater sample to that of water having a salinity of exactly $35^{o}/oo$, where both samples are at the same temperature t, and under a pressure of one standard atmosphere, i.e.,

$$R_t = C(S, t, 0)/C(35, t, 0). \qquad (3)$$

Actually, as discussed by Lyman (1969) and Tsurikova and Tsurikov (1971), the redefinition is actually a reexpression of salinity since it, like Knudsen's titration, is based on the concept of constant composition and is, therefore, still related to Cl as given by (1) or (2).

Most conductivity salinometers measure R_t directly after having established C(35, t, 0) from a Copenhagen Normal Water sample. In situ conductivity-temperature-depth (CTD) sensors, however, measure only C(S, t, p), so in order to use Cox's reexpression of salinity in terms of the conductivity ratio R_t, it is necessary to have available a reliable and standard way to approximate C(35, t, 0). It is to that end that this study is directed.

Salinity Determination from R_t

The pertinent equations proposed by Cox et al (1967) as the international reexpression of salinity as a function of R_t are included below for convenience. R_t is expressed in terms of R_{15}, i.e., at t = 15°C, since most salinometers are temperature compensated to bring the sample to 15°C.

$$S\% = -.08996 + 28.2972R_{15} + 12.80832R_{15}^{2} - 10.67869R_{15}^{3} + 5.9862R_{15}^{4} - 1.32311R_{15}^{5}. \tag{4}$$

For temperatures other than 15°C, they provided a correction factor that is to be added to R_t to get R_{15}, i.e.,

$$R_{15} = R_t + \Delta_{15}(t), \tag{5}$$

where

$$\Delta_{15}(t) = 10^{-5}R_t(R_t-1)(t-15)[96.7 - 72.0R_t + 37.3R_t^{2} - (0.63 + 0.21R_t^{2})(t-15)] \tag{6}$$

Eq. (4) has a range of fit of $4^{o}/oo \leq S \leq 42^{o}/oo$ and (6) has a R. M. S. deviation of fit at 30°C of 0.003% in salinity.

Measurements of C(35, t, 0)

Since Copenhagen Normal Water is the standard used in determining salinity and specifically, since all conductivity salinometers use it to measure the reference value of C(35, t, 0) and calculate R_t, the same standard should be used in providing C(35, t, 0) for use with *in situ* CTD sensors. What is needed, therefore, is a complete set of conductivity measurements for Copenhagen Normal Water over a wide range of temperatures and an equation and table to approximate C(35, t, 0) that fits this data.

To date there apparently has been only two sets of such measurements. Reeburgh (1965) dealt primarily with measurements of the specific conductance of Red Sea Water over a range of chlorinities from approximately $16^{\circ}/oo$ to $22^{\circ}/oo$ and temperatures from -1°C to 35°C. Included in this paper were, except for t = 15°C, a single set of measurements for two Normal Water samples having chlorinities of $19.369^{\circ}/oo$ and $19.372^{\circ}/oo$, respectively. Hassler (1971) measured the specific conductance of Normal Water samples having a chlorinity of $19.3745^{\circ}/oo$ over the range from nearly 0°C to 21°C, but his conductivity values and polynomial coefficients differ significantly from those given by Reeburgh (1965), and Perkin and Walker (1972) (i.e., as much as 2.1 millimho/cm) and no further use was made of them in this study. Other studies, such as Cox et al (1967) and Brown and Allentoft (1966), measured the ratio R_{15} directly.

Approximating C(35, t, 0)

In a recent paper Perkin and Walker (1972) developed a third-order polynomial equation to estimate C(35, t, 0) from the experimental data of Brown and Allentoft (1966), but their intent was to provide an approximation technique for use in the Arctic so their equation is not valid for temperatures greater than 25°C. The use of sensors in lower latitudes would require an equation valid for temperatures greater than 25°C.

For this study, in order to provide a means of approximating C(35, t, 0) over a wide range of temperatures, coefficients of three third-order polynomials were computed by the method of least-squares from the experimental temperature-salinity-conductivity data published by Reeburgh (1965) and shown in Table 1 and Table 2.

The least squares fit of two sets of Reeburgh's Normal Water data was straight forward, but the fit to his Red Sea water data (because the specific conductance was not measured for water having exactly 35°/oo salinity) required a series of additional steps.

In order to insure the best possible fit to this data, the following steps were taken:

(a) for each of the twenty integer values of temperature, a least squares fit between chlorinity and its corresponding specific conductivity was made. The step was necessitated by the fact that the increase in conductivity with increasing chlorinity is not linear, therefore, a simple linear interpolation between known values of conductivity would not be precise, as will be discussed below.

(b) Next, using (2) the chlorinity value (19.37394°/oo) that corresponds to a salinity of 35°/oo was calculated.

(c) Then, for each integer value of temperature, the values of specific conductance that correspond to 19.37394°/oo was obtained using each of the twenty polynomials formulated in step (a). Table 5 shows how these values differ from those obtained for integer temperatures by a linear interpolation of the specific conductances between 19.000°/oo and 20.000°/oo chlorinity.

(d) Finally, using these twenty values of conductance and their corresponding integer temperatures, a least square fit yielded the desired third order polynomial expression for specific conductance at 35°/oo salinity and any t, of the form

$$C(35, t, 0) = A + Bt + Ct^2 + Dt^3. \tag{3}$$

The coefficients A, B, C and D for three temperature ranges are given in Table 3. The R. M. S. deviations of these points from the resulting curves are for Reeburgh's Normal Water less than 0.00212 millimho/cm and for his Red Sea data less than 0.00013 millimho/cm.

Comparison of Results

A comparison of results using the three equations developed from Reeburgh's data and the equation developed by Perkin and Walker (1972) are included in Table 4. Their specific conductance values are under the heading PW; KR, KN_1 and KN_2 come from (3) using the coefficients computed from Reeburgh's Red Sea data and his Normal Sea Water data (Cl = 19.369°/oo and Cl = 19.372°/oo), respectively. Those values marked with an asterick are for temperatures beyond the range of fit of the equation and show the danger of extrapolation beyond that range.

Since the equation developed by Perkin and Walker (PW) also used Reeburgh's Red Sea data for t = 0°C, it is not surprising that the least difference with KR (KR - PW) occurs at this temperature, and what difference there is may be due to the elaboratness of the fit. A systematic increase in the differences is evident for t > 0°C, which is probably a function of the different set of data used in each case.

A comparison of the values of KN_1 minus KN_2 indicate a non-systematic fluctuation in differences, which may in part be because only one set of conductivity measurements were made as a function of temperature for each Normal Water sample. Indeed, if the R. M. S. deviation of fit for each of these two data sets (as shown in Table 4) is examined, there is a strong indication that the measurements of KN_2 may not have been as precise as those of KN_1. The differences, however, when rounded to the nearest hundredth of a millimho/cm are all 0.01 millimho/cm greater for KN_2 than for KN_1 which is consistent with the fact that the salinity of KN_2 is $0.006^{o}/oo$ greater than KN_1. This difference of 0.01 millimho/cm is probably significant only for the best CTD units which have an accuracy greater than ± 0.01 millimho/cm.

A comparison of KR and PW with the two Normal Water samples KN_1 and KN_2 show differences that range from as small as 0.0004 millimho/cm (for KR-KN_1 at t = 0°C) to as large as -0.0224 millimho/cm (for KN_1 - PW at t = 25°C) and -0.0234 millimho/cm (for KR - KN_2 at t = 35°C), the latter two differences being significantly large. Generally KR - KN_1 was markedly less than KN_1-KN_2 and KR - KN_2 was just slightly larger in magnitude, indicating that though Red Sea Water is not necessarily characteristic of oceanic water, diluted to $35^{o}/oo$ salinity it is not significantly unlike it in terms of specific conductance.

Conclusions

The results of this study indicate the need to have established a standard expression for the estimation of C(35, t, 0) for use with CTD sensors. To make it most consistent with current salinity analysis techniques using conductive salinometers and applicable at any latitude, this expression should be derived from a series of measurements made on samples of Copenhagen Normal Water with a chlorinity near $19.374^{o}/oo$ over the temperature range -1°C to 40°C. To establish it as an international standard, the measurements should be under the supervision of the appropriate UNESCO committee.

The conductivity ratio R_t calculated from this standard expression would then be used to obtain salinity using the UNESCO tables or the equation of Cox et al (1967). Instrument differences and measurements made in non-standard composition seawater will still introduce errors as it does using other techniques, but with a standard expression for C(35, t, 0) at least one more variable will have been minimized.

Until the international standard is established, the coefficients listed in Table 3 for Cl = $19.369^{o}/oo$ are suggested as a means of estimating C(35, t, 0).

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Table 1. Specific Conductance of Red Sea Water at Integer Values of Temperature and Chlorinity (Samples A-G). Conductivity in International Millimho/C.M. (Reeburgh, W. S. JMR 23(3), 1965)

	Chlorinity, o/oo						
T°C	16.000	17.000	18.000	19.000	20.000	21.000	22.000
35	53.761	56.744	59.702	62.636	65.548	68.437	71.306
33	51.923	54.807	57.666	60.502	63.317	66.110	68.883
31	50.099	52.884	55.645	58.384	61.102	63.800	66.478
29	48.290	50.976	53.640	56.283	58.906	61.509	64.093
27	46.497	49.086	51.653	54.201	56.728	59.237	61.728
25	44.721	47.213	49.685	52.138	54.572	56.987	59.386
23	42.964	45.360	47.737	50.096	52.437	54.760	57.067
21	41.225	43.526	45.810	48.076	50.325	52.557	54.774
19	39.507	41.714	43.905	46.079	48.237	50.380	52.507
17	37.810	39.925	42.024	44.108	46.176	48.229	50.268
15	36.136	38.159	40.168	42.162	44.142	46.107	48.058
13	34.485	36.418	38.338	40.244	42.136	44.015	45.880
11	32.859	34.703	36.535	38.354	40.160	41.954	43.734
9	31.258	33.016	34.761	36.494	38.216	39.925	41.622
7	29.685	31.356	33.017	34.666	36.304	37.930	39.545
5	28.139	29.726	31.303	32.870	34.426	35.971	37.505
3	26.622	28.127	29.622	31.108	32.583	34.048	35.503
1	25.135	26.560	27.975	29.380	30.777	32.163	33.540
0	24.403	25.788	27.164	28.530	29.888	31.236	32.575
-1	23.679	25.025	26.362	27.689	29.008	30.318	31.619

Table 2. Specific Conductance Measurements for Copenhagen Normal Water Samples (Reeburgh, W. S. JMR 23(3), 1965)

Cl = 19.369°/oo		Cl = 19.372°/oo	
T°C	COND (millimhos/cm)	T°C	COND (millimhos/cm)
35.000	63.738	35.003	63.754
33.001	61.568	32.996	61.573
31.004	59.414	31.003	59.426
30.000	58.341	29.999	58.349
29.000	57.271	29.002	57.282
26.996	55.150	27.004	55.168
25.002	53.057	25.000	53.064
23.000	50.979	22.995	50.979
21.000	48.922	20.994	48.921
20.000	47.905	20.002	47.916
18.999	46.893	19.000	46.902
17.003	44.889	17.000	44.897
15.000	42.908	15.000	42.921
13.001	40.956	12.996	40.964
10.997	39.030	11.000	39.044
10.000	38.083	10.002	38.096
9.000	37.141	9.004	37.156
7.005	35.285	6.998	35.287
5.000	33.452	5.001	33.459
3.000	31.662	2.997	31.669
1.000	29.904	0.995	29.908
0.000	29.039	-0.001	29.043
-1.008	28.176	-0.995	28.192

Table 3. Coefficients for Third-order Polynomials used to Estimate the Conductivity of Seawater of Salinity 35°/oo and Temperature t.

Range of Fit	Coefficients	Data Source
0°C≤t≤35°C	A = 29.03902	Reeburgh - Red Sea Water
	B = 0.85997	Cl = 19.374°/oo,
	C = 0.46993×10^{-2}	S = 35.000°/oo
	D = -0.27221×10^{-4}	
-1°C≤t≤35°C	A = 29.04433	Reeburgh - Normal Water
	B = 0.86141	Cl = 19.372°/oo,
	C = 0.46109×10^{-2}	S = 34.997°/oo
	D = -0.25450×10^{-4}	
-1°C≤t≤35°C	A = 29.03862	Reeburgh - Normal Water
	B = 0.86024	Cl = 19.369°/oo,
	C = 0.46931×10^{-2}	S = 34.991°/oo
	D = -0.27022×10^{-4}	

Table 4. Comparison of Results of Four Equations for Approximating the Conductivity of Seawater that has a Salinity of $35^{o}/oo$

	CONDUCTANCES (millimho/cm)				DIFFERENCES ($\times 10^{-2}$ millimho/cm)					
T°C	KR	PW	KN_1	KN_2	KR-PW	KN_1-KN_2	KR-N_1	KR-KN_2	KN_1-PW	KN_2-PW
35	63.7274	63.7927*	63.7374	63.7508	-6.53*	-1.34	-1.00	-2.34	-5.53*	-4.19*
30	58.3324	58.3740*	58.3399	58.3493	-4.16*	-0.94	-0.75	-1.67	-3.41*	-2.47*
25	53.0499	53.0779	53.0555	53.0637	-2.80	-0.82	-0.56	-1.38	-2.24	-1.42
20	47.9003	47.9216	47.9044	47.9133	-2.13	-0.89	-0.41	-1.30	-1.72	-1.83
15	42.9040	42.9225	42.9069	42.9170	-1.85	-1.01	-0.29	-1.30	-1.56	-0.55
10	38.0814	38.0975	38.0833	38.0941	-1.61	-1.08	-0.19	-1.27	-1.42	-0.34
5	33.4529	33.4640	33.4538	33.4635	-1.11	-0.97	-0.09	-1.06	-1.02	-0.05
0	29.0390	29.0392	29.0386	29.0443	-0.02	-0.57	+0.04	-0.53	-0.06	-0.51

Symbol	Data Source	Range of Fit	R.M.S. Deviation of Fit
KR	Reeburgh - Red Sea	$0^\circ C \leq t \leq 35^\circ C$	0.00013 millimho/cm
KN_1	Reeburgh - Normal Water	$-1^\circ C \leq t \leq 35^\circ C$	0.00100 millimho/cm
KN_2	Reeburgh - Normal Water	$-1^\circ C \leq t \leq 35^\circ C$	0.00212 millimho/cm
PW	Perkin and Walker (Brown and Allentoft)	$0^\circ C \leq t \leq 25^\circ C$	

*Beyond range of fit.

Table 5. Comparison of two methods of determining the specific conductances (in millimho/cm) of Red Sea Water calculated for a salinity of 35^{o}/oo (19.374 Cl^{o}/oo)

T°C	(A) Least Squares	(B) Linear Interpolation	(A – B)
35	63.728	63.725	0.003
31	59.403	59.400	0.003
27	55.148	55.146	0.002
23	50.973	50.971	0.002
19	46.888	46.886	0.002
15	42.904	42.902	0.002
11	39.031	39.029	0.002
7	35.280	35.279	0.001
3	31.661	31.660	0.001
0	29.039	29.038	0.001

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