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THE USE OF ELECTRICAL CONDUCTIVITY MEASUREMENTS FOR CHLORINITY DETERMINATION[1]

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ABSTRACT

Limitations in our knowledge of the electrical conductivity of sea water are discussed. An empirical equation is presented which gives chlorinity as a function of specific conductance and temperature at atmospheric pressure.

Determination of chlorinity of sea water by chemical analysis, while unsurpassed in accuracy, has always been a cumbersome technique and one which generally involves a considerable time lag between sampling and availability of results. An alternative method of determining chlorinity, or salinity, is the measurement of electrical conductivity (specific conductance) as a parameter of chlorinity and of the simultaneously measured temperature. Proof of the basic soundness of this method is furnished by the extended use of the shipboard electrical salinity bridge described by Wenner *et al.* (1930). Its accuracy is considered comparable to that of the Knudsen method of chlorinity titration ($\pm$ 0.02 ‰ of salinity). Since this instrument was designed for empirical calibration against samples of known salinity, the establishment of an exact relationship between specific conductance, chlorinity, and temperature was not required.

Increasing emphasis on *in situ* measurements that result in large quantities of data as well as the desirability of a sound basis of comparison between different sets of specific conductance measurements lend importance to the need for a unique functional relationship between the variables involved. It is the purpose of this note to draw attention to certain limitations in our present knowledge of this relationship and to present an empirical approximation to it which may facilitate the use of this type of data.

The basis for the conversion of most present-day oceanographic measurements of electrical conductivity is a table derived by Thomas *et al.* (1934) from their own experimental work which gives specific

conductance as a function of chlorinity and temperature. From these data Jacobson (1948) developed an analytical function which, because of the approximations involved, is unsuited for accurate work. The only other major investigation of the electrical conductivity of sea water was carried out by Bein *et al.* (1935). Since the objective of Bein *et al.* was a comparison of direct density measurements with values computed from various parameters, their data are presented in a form not readily adaptable to the problem at hand.

The results obtained by Thomas *et al.* appear to contain errors from two sources. One of these, mentioned by the authors in a footnote, is the use of the Parker and Parker (1924) values for the specific conductance of a 0.1 demal potassium chloride solution (the reference standard for their conductivity measurements). Jones and Bradshaw (1933) had found that these Parker and Parker values were low by 0.118% at 0°C, by 0.028% at 18°C, and by 0.028% at 25°C. It can be presumed that the resulting errors in the Thomas *et al.* measurements are of the same magnitude.

The second source of errors is their use of Washburn pipet type conductivity cells. Jones and Bollinger (1931) found that in cells of this general design (Leeds and Northrup Co., 1924) there exists a capacitative shunt between parts of the cells of opposite polarity which results in resistance measurements that are lower than the true values. This so-called Parker Effect varies with the frequency, with the geometry of the cell, and with the resistance of the solution, but it always gives positive errors in conductivity. Although these errors in the Thomas *et al.* data are of unknown magnitude, it is apparent that they are of opposite sign from those due to the reference standards used. Thus the total error in those data might be either positive or negative.

Wenner *et al.* suggest that electrical conductivity may be a more accurate parameter of total salt content than of chlorinity alone. If this is the case, then the Thomas *et al.* data may reflect certain slight geographical differences not only in the conductivity-chlorinity relationship but in the chlorinity-salinity relationship established by Knudsen (1901). Minor anomalies of this nature are indicated, though not conclusively, by the works of Bein *et al.* and of Thompson and Wirth (1931). Jones and Bradshaw pointed out that absorbed carbon dioxide will increase the conductivity of a solution. Since dissolved CO_2 varies over a considerable range in the sea, this effect may be a source of additional small errors in field measurements of specific conductance.

Apparently the effect of pressure on the electrical conductivity of sea water has not been investigated, but it is a factor which cannot be

ignored when dealing with *in situ* measurements at depths of several hundred meters. From analogy with other physical properties of sea water it appears likely that this effect would become significant at a depth which will depend on the degree of accuracy of the measurements.

Despite the various gaps and uncertainties in our knowledge of the electrical conductivity of sea water, it was felt that the development of an analytical function relating specific conductance to chlorinity and temperature at atmospheric pressure would serve a useful purpose. The true physical relationship between these variables should be of the form $C = f(T, H)_{p=0}$, where C = specific conductance in mhos per cm^3 (the dimensions used by Thomas *et al.*; Jones and collaborators use the more conventional mhos per cm), T = temperature in°C, and H = chlorinity in ‰ (halide concentration determined by titration).

From a practical standpoint it is preferable to have a function giving H in terms of C and T. Such an empirical function was derived from the basic experimental data of Thomas *et al.*, and it is believed that it eliminates some slight discrepancies in their results which may well have been due to the above mentioned geographical anomalies.

The simplest form of this relationship is

$$H = \frac{K_1(T)}{C^{-1.07} - K_2(T)},$$

where $K_1(T) =$

$$\frac{6 \times 10^8}{721,392 + 24,597.1T - 29.17T^2 + 20.12T^3 - 0.974T^4 + 0.01584T^5}$$

and $K_2(T) = K_1(T) \times$

$$\frac{5541 + 254.95T + 7.145T^2 - 0.73T^3 + 0.142T^4}{3,904,644}$$

While these two parametric functions of temperature gave the best fit of the data, their complexity may be due partly to the use of the Parker and Parker reference standards whose errors seem to vary rather unsystematically with temperature. In comparing chlorinities computed by means of this equation with the 61 titration values of the original data, the following results were obtained: in 32 cases the difference was 0.002 ‰ or less; in 22 cases it was between 0.003 and 0.005 ‰; and in the remaining 7 cases it varied from 0.007 to 0.027 ‰.

Because of the separation of variables, the above form of the equation lends itself to compact, yet comprehensive, tabulation—one table for each of the three terms. By means of various manipulations it can

be put into other forms which might be more suitable for restricted ranges of the variables or for lower requirements in accuracy.

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