

A CRITIQUE ON CHLORINITY, SALINITY AND ELECTRICAL CONDUCTIVITY INTERRELATIONSHIP OF SEA WATER

C. K. GOPINATHAN AND S. Z. QASIM

National Institute of Oceanography, Panaji, and Central Marine Fisheries Research Institute, Cochin-18

ABSTRACT

Chlorinity in the Cochin Backwater (a tropical estuary) ranges from 0 to 20‰ during the year. Determinations of chlorinity by the conventional titration method and those derived from conductivity measurements using the International Oceanographic Tables differed largely in the range 4-9‰. When the available data on chlorinity, salinity and electrical conductivity from the literature were compared, these were found to differ in a similar manner. The main reason for this difference seems to be that the water from the Baltic Sea has been used for determining the conductivity ratios in the lower range. Probably the calcium-rich river water flowing into the Baltic Sea gives a greater conductance than the sea water diluted by distilled water or by the natural rain water.

INTRODUCTION

In recent years, considerable refinements in the techniques of measurements have improved our knowledge of certain physical and chemical properties of sea water. Salinity is perhaps the best example of such a property.

Many attempts have been made in the past to define salinity or the concepts related to salinity of sea water. The earlier definitions of salinity and chlorinity and the subsequent modification in the definition of chlorinity can be found in any text book of Oceanography (e.g. Sverdrup *et al.*, 1942). However, the salinity so defined has seldom been measured directly; but it is the property like chlorinity expressed by the relationship $S_{\text{‰}} = 1.805 \text{ Cl}_{\text{‰}} + 0.03$ (Knudsen, 1901), which is determined.

For various reasons, such a definition of salinity was not considered satisfactory (Cox, 1963) and thus the need for making it more precise arose. In 1967, a panel of experts defined salinity in terms of chlorinity as $S_{\text{‰}} = 1.80655 \text{ Cl}_{\text{‰}}$ (Wooster *et al.*, 1969). However, salinity was redefined as a function of electrical conductivity ratio (R_{15}), which is the ratio between electrical conductivity of natural sea water and standard sea water of salinity exactly 35‰, both at a temperature of 15°C and a pressure of one atmosphere. This definition was based on the work of Cox *et al.* (1967). For expressing the salinity, these authors fitted a fifth order polynomial in R_{15} , and this finally formed the recommended definition of salinity.

The excellent work of Cox *et al.* (1967) and the redefinition of salinity formed the basis of International Oceanographic Tables Ia, Ib, IIa, IIb (JPOTS, 1966). This definition of salinity, however, created some problems with regard to the concepts of salinity and chlorinity (Lyman, 1969). Tsurikova and Tsurikov (1971) are of the opinion that the salinity defined by Wooster *et al.* (1969) is simply a different expression in terms of dry residue of salinity determined by Forch *et al.* (1902) and not another definition. The problem, according to them, is not yet solved.

Some initial measurements conducted by us showed that there were small differences in the lower range of salinity determined by the conductivity method and that by the conventional titration method. To understand, therefore, the interrelationship between chlorinity, salinity and electrical conductivity more precisely in the lower range, it was considered desirable to collect some preliminary data from an estuarine area where the variations in chlorinity were large. The Cochin Backwater, which is located along Lat. $9^{\circ}58'N$ and Long. $76^{\circ}15'E$, fulfilled our requirements, for the changes in chlorinity in this estuary during the year were of the order of 0-20‰. Thus the measurements on which the following discussion is based were made during the years 1965-67.

The late Dr. R. A. Cox gave us much advice and encouragements when the work was started in 1965 for which we are very grateful. All measurements were carried out at the National Institute of Oceanography, Cochin. We are thankful to Dr. N. K. Panikkar for the facilities for carrying out this work.

MATERIAL AND METHODS

Chlorinity of the water samples collected from the Cochin Backwater was determined by the Knudsen method. At least three determinations were made on each sample with a precision of ± 0.015 ‰. Electrical conductivity of the samples was measured at $28^{\circ}C$ ($\pm 0.01^{\circ}C$), using a conductivity bridge (Toshniwal, Type No. CL 01.02). For these measurements an alternating current of 3000 Hz was used, and the cell connected with the bridge had a constant of approximately 5. The precision in conductivity measurements was greater than 30 micro mhos/cm, or greater than 0.015‰ chlorinity, and the total number of samples measured was 97. These samples covered the entire range of chlorinity from 0 to 20‰.

RESULTS AND DISCUSSION

The relationship between specific conductance and chlorinity has been shown in Fig. 1. The fresh water from the rivers and monsoon rains which diluted the sea water in the estuary had a range in specific conductance from 0.08 to 0.18 milli mhos/cm. The value of specific conductance of the standard sea water at $28^{\circ}C$ measured by our bridge agreed very closely with the value given by Reeburgh (1965). A small correction incorporated to this value gave the specific conductance of the standard sea water of salinity 35‰, which was used for converting the values of the sample to conductivity ratios at $28^{\circ}C$. Using the International Oceanographic Tables IIa and IIb, these ratios were converted into salinity and subsequently into chlorinity, as desired.

The chlorinity determined by the titration method and that computed from the conductivity ratio differed mainly in the lower range of chlorinity, below 16.5‰. Fig. 2a gives the mean differences in chlorinity at each 1 Cl‰ interval. The difference between the two sets of values was maximum in the chlorinity range 4-9‰. This gave an indication that in the lower range, the samples from the backwater had a lower conductance than that of the samples measured by Cox *et al.* (1967) for that range. This difference prompted us to investigate the problem in greater detail.

[2]

For comparison with our measurements, the best available data in the literature are those of Brown and Allentoft (1966) and Cox *et al.* (1967). The precisions,

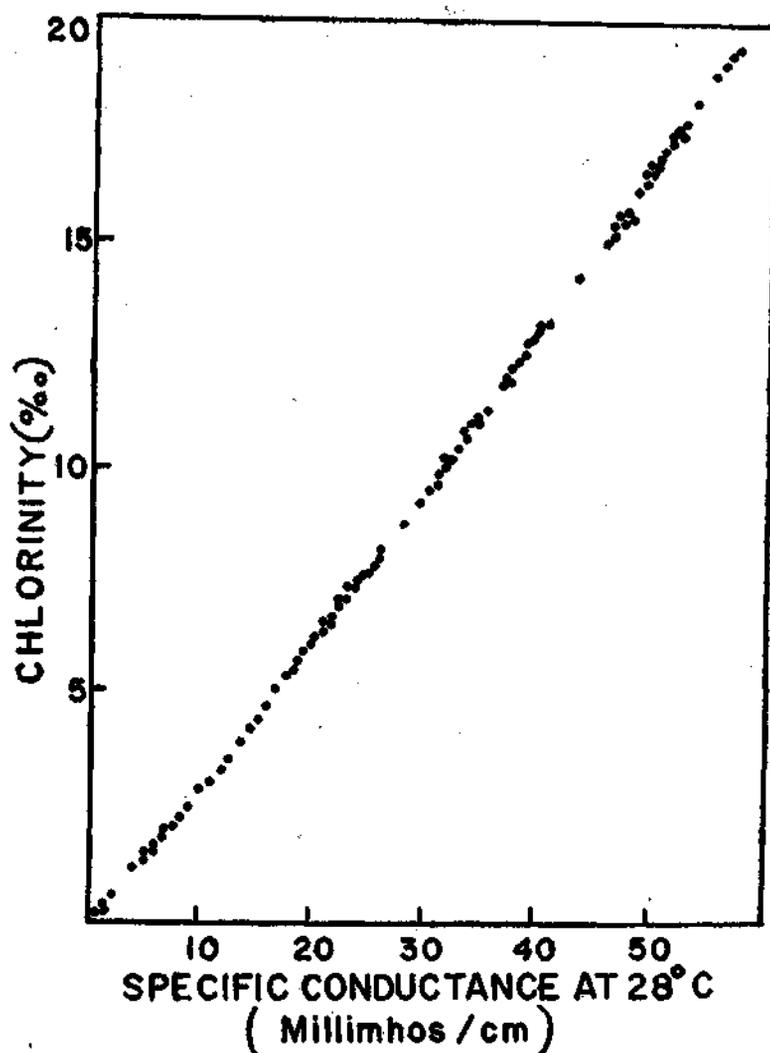


Fig. 1. The relationship between chlorinity and specific conductance at 28°C in the samples taken from the Cochin Backwater.

however, of the measurement of salinity and conductivity ratios of Brown and Allentoft and Cox *et al.* are far greater than those of our measurements. Brown and Allentoft (1966) used pure de-ionised distilled water for diluting the sea water, and a high precision technique for the measurement of conductivity ratios. Their salinity values can easily be converted into chlorinity by using the formula $S‰ = 1.80655 Cl‰$. It is also possible to use the conductivity ratios of Brown and Allentoft to get the salinity values from the International Oceanographic Tables. These can also be converted into chlorinity by using the above formula.

Fig. 2b gives the differences in chlorinity at regular intervals. It is clear from the figure that the values differ in a systematic manner. The maximum difference of more than 0.02 Cl‰ was found in the chlorinity range 4 to 8‰. This observation would also indicate that the water sample used by Brown and Allentoft (1966) had a lower conductance than those of Cox *et al.* (1967) throughout the chlorinity range 1-18‰. The peak difference was at about 6‰ (Fig. 2b).

The only other available data for comparison in the lower range of chlorinity are of Thomas *et al.* (1934). Their samples again were not natural, but were made by diluting the sea water with distilled water. According to Reeburgh (1965), they measured chlorinity in terms of chlorine-equivalent. However, their values can be corrected by using the ratio of chlorine-equivalent to chlorinity as given by Lyman and Fleming (1940). Pollak (1954) pointed out that the conductivity measurements of Thomas *et al.* at 25°C are low by 0.028% because they used the wrong value of conductivity standard. However, due to the Parker Effect in the measurements the values become slightly high and hence the combined effect of the two errors in the conductivity measurements becomes of some unknown magnitude. Reeburgh (1965) found a fair agreement between his conductivity values and those of Thomas *et al.* from which it can be assumed that the total error in the conductivity values of Thomas *et al.* is small. Their conductivity values at 25°C can be converted into ratios by using the conductivity data of standard sea water of salinity 35‰ from Reeburgh (1965). Thus, it is once again possible to get the corrected chlorinity values and also chlorinity values from the conductivity data using the International Oceanographic Tables. The differences between these have been shown in Fig. 2c. The samples of Thomas *et al.* (1934) also seem to give less conductance than that of the natural samples of Cox *et al.* (1967). Here the difference is throughout the chlorinity range, with a peak at about 6 Cl‰.

The chlorinity values of Cox *et al.* (1967) can also be compared with those derived from the conductivity ratios using the International Oceanographic Tables. The differences between the two sets of values have been shown in Fig. 2d. To establish salinity-conductivity relationship, Cox *et al.* analysed 135 samples of natural sea water. Only 20 samples were in the chlorinity range less than 16.5‰ (salinity less than 30‰). Of these, 15 samples were obtained from the Baltic Sea. From the works of Grasshoff (1965) and Kwiecinski (1965) the peculiarity in the chlorinity/conductivity relationship of the Baltic water is well known. Grasshoff (1965) reported the intercalibration measurements conducted at Copenhagen in June 1965, when 7 water samples from the Baltic were analysed a number of times by 4 different institutions for salinity and chlorinity. Salinity was determined by salinometers and chlorinity by the conventional titration method. The precision of chlorinity determination was $\pm 0.018\%$ and that of salinity about 0.01‰. The mean differences in chlorinity determined directly and that derived from the conductivity measurements are shown in Fig. 2e. Chlorinity computed from the conductivity was higher in the range 1-10 Cl‰, with a maximum (0.028‰) in the chlorinity range 3-5‰. Similar differences were obtained by Kwiecinski (1965) in the surface samples of the Baltic Sea, which, being rich in calcium, gave a greater conductance. Probably the river water flowing from the Central Europe into the Baltic gets rich in calcium and thus gives rise to this peculiar property.

From the analysis presented in Fig. 2, it seems that the difference between the data of Brown and Allentoft (1966) and Cox *et al.* (1967) is probably because the latter authors used water samples of lower salinities from the Baltic Sea.

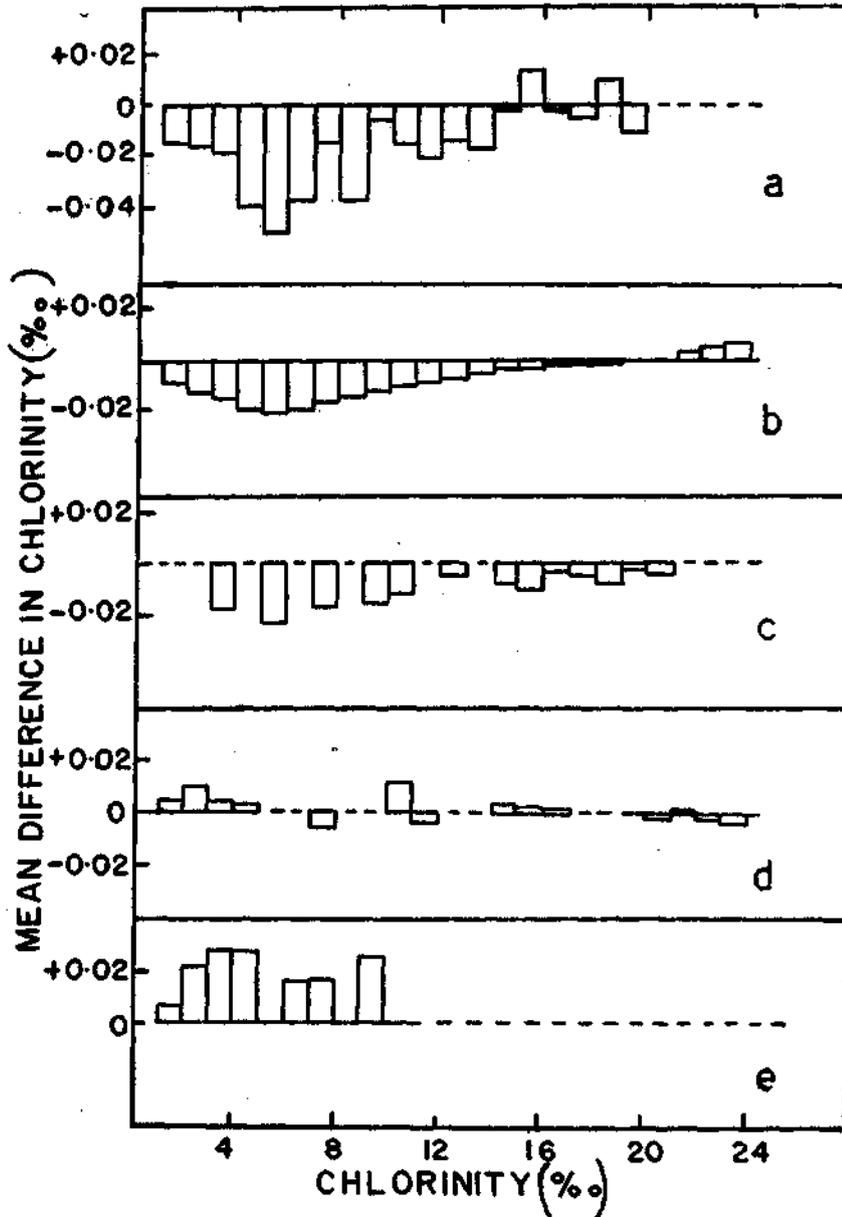


Fig. 2. Differences obtained at various chlorinity values between direct determinations and those computed from conductivity values. In a-d chlorinity was computed from conductivity by using the International Oceanographic Tables. a. In samples from the Cochin Backwater; b. In samples of Brown and Allentoft (1966); c. In samples of Thomas *et al.* (1934); d. From the data of Cox *et al.* (1967); e. From the analysis of Baltic water by Grasshoff (1965). Salinity determined by salinometer was converted into chlorinity by Knudsen formula.

One of the reasons for redefining salinity was that in the Knudsen equation ($S‰ = 1.805 Cl‰ + 0.03$), the value of 0.03 represented approximately the solid material contained in the fresh water flowing into the Baltic Sea (UNESCO, 1966). Thus the equation has some significance when it was used as an arbitrary method of determining salinity. At present there is no evidence available to show that the conductivity at lower chlorinity range in other parts of the world would correspond to that found in the Baltic Sea. Tsurikova and Tsurikov (1971) have pointed out that the continental drainage water flowing into the oceans may have a different chlorinity/salinity relationship. They stated that at 5 Cl‰, the disparity between the actual salinity value and that calculated from the equation of Wooster *et al.* (1969) would be of the order of 0.16‰. Under such situations, what Tsurikova and Tsurikov (1971) have termed as 'local effect', the use of an arbitrarily defined relationship becomes questionable.

The International Oceanographic Tables do not cover the salinity range below 2.85‰. For salinity less than 1‰, direct chlorinity estimates would give the best indication of the sea water fraction contained in the sample (Mangelsdorf, 1967), but the conductivity values will give the best indication of the total dissolved solids. Except for the Baltic waters, nothing is known of the chlorinity/conductivity relationship of natural samples of chlorinity less than 16.5‰. The conductivity values of the samples from the Cochin Backwater agree closely with those of Brown and Allentoft (1966). Since in most measurements, the difference in chlorinity has been found to be in the lower range (Fig. 2), it seems desirable to investigate whether these differences arise because Baltic water has been used in earlier measurements or whether there is a regional difference in chlorinity, salinity and conductivity interrelationship associated with the natural water which dilutes the sea water.

REFERENCES

- BROWN, N. L. and ALLENTOFT, B. 1966. *Salinity, conductivity and temperature relationships of seawater over the range of 0 to 50 P.P.T., Final Report, March 1, 1966.* Prepared for United States Navy Office of Naval Research. Contract NOnr-4290(00), M.J.O. No. 2003. Bissett-Berman Corporation, California. 60 pp.
- COX, R. A. 1963. The salinity problem. pp. 243-261. In: M. Sears (ed.) *Progress in Oceanography*, Vol. I. Pergamon Press, London.
- , CULKIN, F. and RILLEY, J. P. 1967. The electrical conductivity/chlorinity relationship in natural sea water. *Deep-sea Res.*, 14: 203-220.
- FORCH, C., KNUDSEN, M. and SORENSEN, S. P. C. 1902. Berichte über die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen. *D. Kgl. Danske Vidensk. Selsk. Skriffter*, 6 Raekke, *Naturvidensk. og Mathem.*, 12: 1-151.
- GRASSHOFF, K. 1965. The results of the intercalibration measurements during the informal meeting in Copenhagen. pp. 6-8. In Report on the intercalibration measurements in Copenhagen, 9-13 June 1965. *UNESCO technical papers in marine science*, No. 3.
- JOINT PANEL ON OCEANOGRAPHIC TABLES AND STANDARDS. 1966. *International Oceanographic Tables.* UNESCO Publications Centre, New York, 118 pp.
- KNUDSEN, M. 1901. *Hydrographical Tables.* G.E.C. Gad, Copenhagen. 63 pp.
- KWIECINSKI, B. 1965. The relation between the chlorinity and the conductivity in Baltic water. *Deep-Sea Res.*, 12: 113-120.
- LYMAN, J. 1969. Redefinition of salinity and chlorinity. *Limnol. Oceanogr.*, 14: 928-929.

CHLORINITY, SALINITY AND ELECTRICAL CONDUCTIVITY OF SEA WATER 299

- LYMAN, J. and FLEMING, R. H. 1940. Composition of sea water. *J. Mar. Res.*, 3 : 134-146.
- MANGELSDORF, P. C. JR. 1967. Salinity measurements in estuaries, pp.71-79. In : G. H. Lauff (ed.) *Estuaries*. American Association for the Advancement of Science, Publication 83, Washington, D.C.
- POLLAK, M. J. 1954. The use of electrical conductivity measurements for chlorinity determination. *J. Mar. Res.*, 13 : 228-231.
- REEBURGH, W. S. 1965. Measurements of the electrical conductivity of sea water. *Ibid.*, 23 : 187-199.
- SVERDRUP, H. U., JOHNSON, M. W. and FLEMING, R. H. 1942. *The oceans, their physics, chemistry and general biology*. Prentice Hall Inc., New York. 1087 pp.
- THOMAS, B. D., THOMPSON, T. G. and UTTERBACK, C. L. 1934. The electrical conductivity of sea water. *J. cons. int. Explor. Mer*, 9 : 28-35.
- TSURIKOVA, A. P. and TSURIKOV, V. L. 1971. On the concept of 'Salinity'. *Oceanol.*, 11 : 282-286.
- UNESCO. 1966. Second report of the joint panel on oceanographic tables and standards. *UNESCO technical papers in marine science No. 4* : 9 pp.
- WOOSTER, W. S., LEE, A. J. and DIETRICH, G. 1969. Redefinition of salinity. *Limnol. Oceanogr.*, 14 : 437-438.