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Chlorinity Determination in Estuarine Waters by Physical Measurement

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ABSTRACT

The differential refractometer has been used as an effective instrument for chlorinity determination. Results obtained through its application have been compared with those derived from the use of less sensitive refractometers and with those obtained from specific conductivity measurements. The advantages of differential refractive-index measurements when applied to water in an estuarial brackish marsh basin are demonstrated. Specific conductance measurements proved to be unreliable in determining chlorinity for such waters; on the other hand, initial studies indicate the feasibility of utilizing differential refractive-index measurements.

It is suggested that, with appropriate calibration procedures at suitable wave lengths, differential refractive-index measurements may provide a quick and easy method for determining the chlorinity of clear ocean water with an accuracy that is satisfactory for most investigations.

Introduction. In characterizing chemically the waters from marsh areas in Lafourche Parish, Louisiana, a chemical method of determining chlorinity was replaced with one based on physical measurements that provided more satisfactory results. From physical and chemical data collected early in our study, it was observed that the often-used specific conductance method gave erroneous results in many instances whereas the differential refractive-index method gave reliable results. It is the purpose of this paper to show the usefulness of the latter method in determining the chlorinity of such waters and to discuss the inadequacy of specific conductance measurements for this particular purpose.

Routine determination of chlorinity with physical methods has been limited primarily to density, specific conductance, and refractive-index measurements. The density method was abandoned by us because it gave low accuracy for these waters, consumed much time, and required accurate temperature measurement and control.

Although the specific conductance measurement has been widely used in recent years, it has proved unsatisfactory in our work. Wenner et al. (1930) described a conductivity instrument (for use aboard ship) that gave results comparable to Knudsen's titration method; modified versions of this apparatus are used today by the U.S. Coast Guard. Thomas et al. (1934) studied electrical conductivity as a function of chlorinity and temperature and presented interpolation formulae for specific conductance as a function of chlorinity at various temperatures. Errors in the latter work and limitations in our knowledge of the electrical conductivity of seawater were discussed by Pollak (1954). In recent years, several instruments for measuring electrical conductivity *in situ* have been described by Jacobson (1948), Reid and Clayton (1952), and Carritt (1952).

Although the refractive-index method has not been widely used, it has been studied by several investigators. Using seawater diluted with distilled water, Utterbach et al. (1934) studied the variation of refractive index with chlorinity at five-degree temperature intervals from 0° to 25° C; these workers used a Bausch and Lomb Dipping Refractometer, which has an accuracy of $\pm 7.0 \times 10^{-5}$ in η and a refractometer temperature control of $\pm 0.02^\circ$ C. They found a linear relationship that could be expressed by $\eta_t = \eta'_t + b \cdot Cl$, where η_t is the refractive index of seawater samples at temperature t , η'_t the refractive index of distilled water at the same temperature, and b a constant appropriate for that temperature. Miyake (1939), working with artificial seawater, showed that its refractive index is the sum of the refractive indices of the individual ions. Using the Lorentz (1880) and Lorenz (1880) equations for equivalent refraction, Miyake was able to calculate from the refraction of the individual ions a value that agreed with the experimentally determined value. The Pulfrich refractometer used by Miyake has an accuracy of 1×10^{-5} in η . Miyake worked at 25° C but he did not indicate with what precision temperature was controlled.

Sampling Area. Water samples used in this study were collected from a 6 × 18-mile section of brackish marsh located in a western portion of Lafourche Parish, Louisiana. This section, bound on the east and west by old natural levees and on the south by a large saltwater bay, is fed from the north by several small intermittent freshwater streams. Several navigable bayous, varying in depth from two feet in the northern portion to 12 feet in the southern portion, traverse the area. A number of shallow lakes and bays, most of which contain active oyster beds, spot the marsh. This area is subject to diurnal tides that have a maximum range of two feet. When southerly winds prevail, almost the entire area is inundated with brackish water, and when northerly winds prevail, large mud flats are exposed in the lakes and bays. Under normal conditions there is a pronounced chlorinity gradient from north to south. Four sets of samples, taken at three-

month intervals, were collected at 24 established stations located throughout the area.

Sampling procedures. Water samples for the determination of chlorinity, specific conductivity, and differential refractive index were collected with a Foerst Water Sampler at a depth of 2 to 3 feet below the surface. The samples were tightly sealed in screw-cap glass bottles and returned to the laboratory for analysis. They were protected from direct sunlight and were stored at room temperature until analyzed.

Experimental Methods and Apparatus. The well-known Mohr volumetric procedure as adapted for seawater was used in determining chlorinity ($\pm 0.02\%$).

A Leeds and Northrup Portable Conductivity-Resistivity Indicator and a Washburn-type Conductivity Cell that had a cell constant of approximately 1 cm^{-1} were used to measure the specific conductivity of undiluted samples. During determinations, the conductivity cell was immersed in a thermostatically controlled water bath to obtain a temperature of $15^\circ \text{C} \pm 0.05^\circ$; readings were taken at five-minute intervals until thermal equilibrium was indicated.

Refractive indices were determined with a Brice-Phoenix Differential Refractometer, which has a limiting sensitivity of $\pm 2 \times 10^{-6}$ in $\Delta\eta$ (difference between refractive index of sample and solvent—distilled water) and has a range of difference of about 0.01. Two monochromatic light sources were employed: a mercury lamp with a green filter transmitting at $547 \text{ m}\mu$ and a sodium lamp transmitting at $589 \text{ m}\mu$. Water twice distilled was used as the reference solvent. During evaluation of temperature dependency and determination of the dilute seawater reference curve, the cell-compartment temperature was maintained constant by circulating water from a thermostated water bath. Most measurements on samples taken from the field were made at room temperature, at approximately 25°C .

Data and Discussion. Fig. 1 shows a plot of chlorinity data ($\%$) versus specific conductance data ($\text{mhos} \times 10^3$) obtained during the first quarterly survey; it shows also a reference curve (dashed line) calculated from the equation by Thomas et al. for specific conductance of seawater at 15°C . The plot for this quarterly survey (solid line) fitted the scattered points (individual observations) rather poorly at best and varied in numerical value of slope from 0.45×10^3 to 0.61×10^3 for the four quarterly surveys. Thus conducting species other than the chloride ion altered the specific conductivity to an extent depending on physical conditions in the area at the time of measurement; other factors presently unknown may have altered it also. This indicates that a standard conductance curve for the determination of chloride could not be prepared for a given area based on one sampling trip, nor could it be applied with better than 20–30% accuracy at some later date.

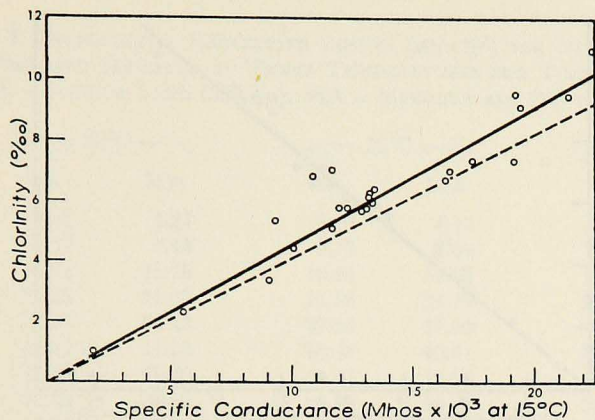


Figure 1. Chlorinity versus specific conductance (mhos $\times 10^3$ at 15°C , $L^{15^\circ\text{C}}$). Solid line, experimental points for the first quarterly survey at 24 sampling stations in the area; chlorinity = $0.45 \times 10^3 L^{15^\circ\text{C}}$. Dashed line, theoretical curve for open seawater calculated from the equation of Thomas et al.; $L^{15^\circ\text{C}} = 2.7009 \times 10^{-3} \text{Cl} - 5.1390 \times 10^{-5} \text{Cl}^2 + 2.097 \times 10^{-6} \text{Cl}^3$.

Also, the spread of points on the specific-conductance-versus-chlorinity plot indicates that some locations are already under variable influences that contribute or take away conducting species other than chlorides; i.e. conductivities are variably higher or lower than can be accounted for by the chlorinity variations only. Under these influences, other electrolytes are in variable ratio to the chloride ion. We refer specifically to the variable influx of brine from oil wells within the area and to variations caused by an influx of fresh water with its suspended and dissolved conducting materials. Assuming a conductivity method for chloride throughout the area on any single day, average errors in chlorinity of the order of 10% to 15% might be expected.

The difference in slope of each curve for our four surveys as well as the discrepancy between the curve for open ocean waters and those for estuarine waters (obtained experimentally by us) are readily recognized. In view of these observations, the use of specific conductance as a means of determining chlorinity in these waters was abandoned.

Fig. 2 shows chlorinity plotted against the differential refractive index ($\times 10^4$ at 25°C) for our first quarterly survey; the slope of the line is 3.20×10^3 . The average slope for the four quarterly surveys was $3.24 \pm 0.05 \times 10^3$, and the slopes of the four separate calibration curves differed from their mean throughout the year by only 1.2%. The correlation between the two properties was high enough so that the maximum error in applying this method for the determination of chlorinity would have been 6% while the mean error would have been less than 2% in 92 of the 96 samples. If a determination of chlorinity from a measurement of the differential refractive index is desired, then the chlorinity at one location should be determined by chemical

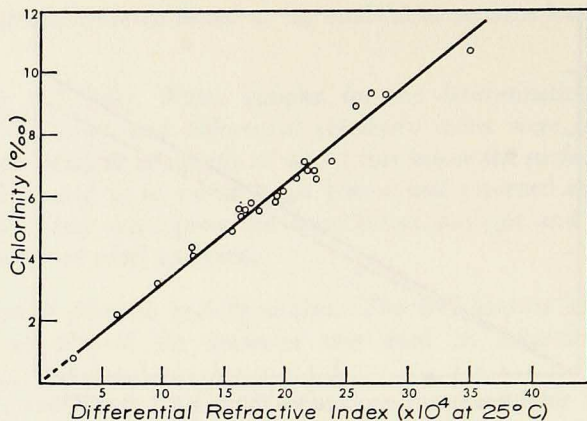


Figure 2. Chlorinity versus differential refractive index ($\times 10^{-4}$ at 25°C). Experimental points for the first quarterly survey at 24 sampling stations in the area; chlorinity = 3.2×10^{-3} D.R.I.

analysis and a curve with a slope of 3.24×10^3 should be drawn through this point, with chlorinity (‰) as the ordinate and with the differential refractive index ($\times 10^4$) as the abscissa. This resultant slope is higher than the value obtained for diluted seawater by Utterbach et al. (3.05×10^3) or by Miyake (2.99×10^3).

In order to check both method and apparatus, ten samples ranging from 0 to 19.38‰ were prepared from standard seawater with twice-distilled water. The differential refractive indices in Table 1 were determined at 20° , 25° , and 30°C with two light sources, one being an accepted standard and the other a more intense source for easier reading in routine work. A plot of the data obtained with the sodium lamp at 25°C (data in Table 1) gave $\Delta\eta = 3.33 \times 10^4 \text{ Cl}/\text{‰}$, which agrees with the corresponding value of 3.34×10^{-4} obtained by Miyake. To compare further our data with those of Miyake, values of $\Delta\eta$ for different chlorinities, calculated from the respective line slopes, were compared with experimentally determined values. The standard deviations were $\pm 0.242 \times 10^{-4}$ for nine samples in our work and $\pm 0.532 \times 10^{-4}$ for ten samples in the study by Miyake.

In Table 1, additional data are given for samples prepared from seawater and distilled water. Comparison of plots for the differential refractive index against chlorinity for the three different temperatures shows a slight shift in line slope. In order to ascertain how much of the shift resulted from temperature differences, the precision of the differential refractometer measurements was evaluated. Each datum entry in Table 1 is the average of two sets of readings (5 measurements per set) taken by two separate operators. The data taken by the two operators agreed within a mean difference of -0.04×10^{-4} and provided a standard deviation of $\pm 0.07 \times 10^{-4}$. The temperature coefficient

TABLE I. DIFFERENTIAL REFRACTIVE INDICES ($\Delta\eta \times 10^4$) FOR NINE SOLUTIONS OF STANDARD SEAWATER AT THREE TEMPERATURES AND TWO WAVE LENGTHS. SL = SODIUM LAMP (589 $m\mu$), MA = MERCURY ARC (547 $m\mu$).

Cl $\%$ / ∞	20°C		25°C		30°C	
	SL	MA	SL	MA	SL	MA
1.21	4.23	4.27	4.19	4.17	4.10*	4.11*
2.42	8.37	8.43	8.33	8.34	8.23	8.27
4.84	16.62	16.76	16.48	16.62	16.28	16.41
7.27	24.86	25.08	24.58	24.79	24.32	24.57
9.69	32.88	33.18	32.55	32.80	32.32	32.62
12.11	40.87	41.28	40.46	40.81	40.17	40.59
14.54	48.89	49.40	48.41	48.96	48.18	48.64
16.96	56.88	57.55	56.39	56.84	56.10	56.59
19.38	64.77	65.45	64.06	64.75	63.84	64.36

* Data taken from a plot of $\Delta\eta$ versus concentration at 30°C. At this temperature and concentration, evaporation in the refractometer cell caused the actual values to be high by about 5%.

of the differential refractive index is small (ca. 0.05×10^{-4} per degree at 25°C), so temperature control within several degrees is sufficient for reasonably accurate determination of chlorinity. The thermal coefficient of the differential refractive index is really concentration-dependent. This is an observation that offers interesting possibilities for further study.

The difference in reliability of chloride determinations obtained from measurement of specific conductance and from the differential refractive index can be interpreted in the light of Miyake's study with artificial seawater and from our own observations. Specific conductance is dependent on all ions present in solution, and that portion of the current carried by any one ionic species is dependent upon its charge, relative mobility, and concentration. Although the chloride ion is the most abundant cation present, the other ions, colloidal material, and weakly ionized organic matter in the solution will collectively reduce to an unknown extent the relative amount of current carried by the chloride ion. In contrast, Miyake has shown that up to 90% of the ionic refraction is due to the chloride ion alone. Consequently, chloride concentration can be more precisely related to differential refractive index than to specific conductance.

Before differential refractive-index measurements can be used to determine chlorinity in a particular area of estuarine inshore waters, additional data must be collected to ascertain the slope of the line for the differential refractive index against chlorinity in that area. Dilute seawater may not be used as a standard. However, differential refractive-index determinations can give a rapid and highly accurate method of determining the chlorinity of clear ocean water, probably from a universal reference curve. Since highly accurate tem-

perature control is not needed, the new flow-type differential refractometers, available in either indicating or recording models, could provide a rapid method of routinely processing numerous samples.

REFERENCES

- CARRITT, D. E.
1952. Oceanographic instrumentation. Publ. Natl. Acad. Sci.-Natl. Res. Council., 309: 172-176.
- JACOBSON, A. W.
1948. An instrument for recording continuously the salinity, temperature and depth of sea water. Trans. Amer. Inst. elect. Engrs., 67 (1): 714-722.
- LORENTZ, H. A.
1880. Ueber die Beziehung zwischen der Fortpflanzungsgeschwindigkeit des Lichtes und der Körperdichte. Ann. Phys., Leipzig, 9: 641.
- LORENZ, L. V.
1880. Ueber die Refractionsconstante. Ann. Phys., Leipzig, 11: 70.
- Miyake, Yasuo
1939. Chemical studies of the western Pacific Ocean in the refractive index of sea water. Bull. chem. Soc. Japan, 14 (6): 239-242.
- POLLAK, M. J.
1954. The use of electrical conductivity measurements for chlorinity determination. J. mar. Res., 13: 228-231.
- REID, R. O., AND W. H. CLAYTON
1952. Progress report 15 March, 1951 to 14 March, 1952. Texas A. and M. Res. Found., ONR Contract N7ONR-487, project NR 084-004: 8-9.
- THOMAS, B. D., T. G. THOMPSON, AND C. H. UTTERBACH
1934. The electrical conductivity of sea water. J. Cons. int. Explor. Mer, 9: 28-35.
- UTTERBACH, C. L., T. G. THOMPSON, AND B. D. THOMAS
1934. Refractivity-chlorinity-temperature relationships of ocean waters. J. Cons. int. Explor. Mer, 9: 35-38.
- WENNER, FRANK, H. SMITH, AND F. M. SOULE
1930. Apparatus for the determination aboard ship of the salinity of sea water by the electrical conductivity method. Bur. Stand. J. Res., Wash., 5: 711-732.