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A SALINOMETER FOR USE IN BRACKISH WATER

BY

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In principal this salinometer is a "battery" composed of a pair of dissimilar metals immersed in the brackish water of the field as an electrolyte. Between these dissimilar metals there exists a potential difference which is practically independent of the concentration of salts in the electrolyte over a very wide range. However, the salt concentration has a marked effect upon the conductivity of the electrolyte. If the measuring circuit has constant resistance, the only change of resistance in the total circuit is that due to the change of conductivity of the water in which the cell is immersed. Since the driving EMF is essentially constant, the current flowing in the circuit is a measure of the conductivity of the water sample.

The conductivity of salt solutions varies with both salt concentration and temperature, an increase of either quantity in dilute solution producing an increase in conductivity. Fortunately there is a way to neutralize the changes of conductivity due to changes of temperature, leaving only those due to changes of salinity. Aqueous salt solutions have a negative temperature coefficient of resistance while most metals have a positive one. It is a simple matter, therefore, to place in series with the cell and in thermal contact with the water a wire resistor having a positive thermal coefficient and a numerical change of resistance both equal and opposite to that of the water sample. This method of temperature compensation is not exact for all salinities, since the temperature coefficient of resistance of salt solutions changes with the salt concentration, but the errors are small. A midrange salinity can be chosen in accordance with the demands of the field problem and the change of resistance ($\Delta R$) of the cell measured over the range 0 °C., to 30 °C.; ($\Delta T$). Knowing $\alpha$, the temperature coefficient of resistance for the metal wire compensator, one can calculate the room temperature resistance ($R_o$) needed to compensate the cell.

$$R_o = \frac{(\Delta R)}{\alpha (\Delta T)}$$

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Figure 36. (Left)—Side view showing part of 50 feet of cable, underwater unit, and the stowage compartment for both. The temperature compensating resistor winding is on top of the disc-shaped underwater unit. The complete instrument weighs 22 pounds and occupies less than one cubic foot of space. (Right)—Front view showing the salinity indicator (white dial), the polarization current indicator (black dial), with the calibration knob between. In the lower bank (left to right) are polarization current limiter, battery switch, salinity indicator switch, reading switch, and the range selector. Note the calibration chart in the lid, as well as the ring electrodes and perforations in the underwater unit.

Nickel wire 0.010 inches in diameter, having an $\alpha = 0.006 \text{ ohms/}^\circ \text{C.}$, has been found most suitable. The cell itself can be built of practically any combination of metals or substances susceptible to strong and lasting polarization, such as Carbon. Experiments with many combinations show Copper and Zinc to be electrically and chemically suitable. The physical shape of the Cu-Zn pair is relatively unimportant and may be altered to suit the requirements of the investigation.

A problem presented to the writer was the measurement of the salinity of thin layers of terrigenous fresh water floating on, and mixing with, sea water in a small estuary which was being used for ecological studies (Edmondson, 1947). The electrode shape finally chosen was a pair of concentric horizontal rings a few millimeters in height. These, together with a flat ring of lucite on which the compensating resistance wire was wound, produced a cylindrical underwater unit.
1 cm. high and 10 cm. in diameter which was so thoroughly pierced with large holes that it disturbed the water only slightly when lowered through the boundary between stratified water layers. Through efforts to maintain lowest possible cell resistance, it was found that twice as much Zinc surface as Copper surface was needed. For this reason the outer ring was made of Zinc and the inner one of Copper.

This ratio of areas is also found to be best in the case of flat plates. Long narrow plates are more efficient than square ones. Efficiency is gauged in terms of the largest current passed through the measuring circuit when comparing electrodes of the same area and spacing but different shape. Long narrow electrodes also have the least “surface error”: specifically, a reduction of current in the measuring circuit due to the electrodes being quite near the liquid surface boundary across which the ion field cannot develop. Electrodes having an aspect ratio greater than 10 to 1 can be brought within 0.5 of a ratio unit of the surface before surface effects become serious. This is less than the practical limit, since the temperature compensator is then out of water.

The preparation and use of Copper-Zinc electrode pairs involves a simple preliminary technique. A new Copper-Zinc electrode pair immersed in a saline solution develops an EMF instantly, but the current flowing between the plates is subject to rapid change, ultimately subsiding to a vanishing quantity. This is due to the insulating effects of the reaction products on the plates through which most of the initial potential drop is eventually consumed. To avoid this effect an outside EMF, larger than that of the cell, is applied to drive the cell backward producing a copious emission of bubbles (H₂) at the Zinc plate. Thirty seconds of treatment at one ampere prepares the electrodes for use. During the counter polarization treatment a number of compounds are developed on both electrodes (Bengough and May, 1924). The Zinc electrode is oxidized and eventually develops a white coating of ZnCO₃ upon exposure to air. The Copper electrode at first becomes yellow with CuCl₂, Cu₂O and, in the presence of sufficient oxygen, Cu₄(OH)₆Cl₂ · H₂O, turning yellow-green and finally blue-green upon exposure to air. The final coating is mossy or slightly botryoidal, its color being determined by the preponderance of Malachite CuCO₃ · Cu(OH)₂ [the basic Cupric Carbonate developed in the presence of atmospheric CO₂], and Cupric Oxychloride CuCl₂ · 2 CuO · 4 H₂O.

After preparation the behavior of the electrodes is quite changed, as is shown in Fig. 37. Upon immersion in the water sample the current at first falls off rapidly, then more slowly, and finally, in a matter of 10 seconds all told, it assumes a constant value which is maintained for several minutes before beginning the asymptotic decline toward
The plateau value is the one which is useful in salinity measurement. It is thought that this plateau is produced by the slow solution of the chemical products of counter-polarization. The plateau lasts longer in high salinity water than in low, suggesting that the rate of solution is controlled by the concentration of salts around the electrodes. Counterpolarization is complete when the current output of the electrodes, immediately after recharging, has a plateau in its time rate of decline. The plateau results from a certain number of coulombs of charge having been passed backwards through the cell. The length of the plateau in time is not conspicuously increased by an overdose of charge but the time required for the plateau to be reached is measurably increased. For this reason it is helpful to place an ammeter in series with the counterpolarizing EMF. Its reading is at first 10 per cent higher than later, a sudden drop indicating when the counterpolarization process is complete.

The salinometer circuit, including that of the underwater unit, is given in Fig. 38. The principal control is the “reading switch,” a double-throw, single-pole switch that automatically cuts out the salinity-indicating milliammeter whenever the counterpolarizing current is cut in. Calibration is accomplished by means of a variable resistor in series with the salinity indicator. A bottled sample of water of known salinity must be carried along for calibration purposes. After the underwater unit has been counterpolarized for a minute or so to
insure the restoration of the deposits on the electrode surfaces and their thorough saturation with water, the reading switch is thrown and the system is allowed to come to equilibrium in the calibration sample. By adjustment of the resistance of the reading circuit the milliammeter can be made to read properly the salinity of the known sample based upon the original calibration curve made in the laboratory from a series of other known samples. In the field, calibration at only one point is sufficient to bring the whole scale of values into proper alignment. Recalibration is desirable every now and then to be sure that mechanical shifting caused by inadvertent bumping of the instrument, or the sun’s heat, has not changed the preliminary calibration.

The calibration curve for the instrument is exponential in appearance, but it follows no true exponential function as far as is known. A family of such curves for different temperatures is shown in Fig. 39. These curves were determined by cutting a sample of sea water of pre-arranged temperature and known salinity with fresh water at the same temperature, counterpolarization having been standardized at 15 seconds and applied before each reading. The cuts were made in the ratios 1/1, 1/2, 1/4, 1/8, 1/16, 1/32, these being successive cuts each by
Figure 39. Characteristic Calibration Curves for Various Temperatures.

Figure 40. Residual Errors Including Reading Error After Temperature Compensation at 20° C. and 16°/oo.
half of an original volume. With a temperature compensated cell only one or two such runs need be made, and these without excessive attention to temperature. It will be noted that the shape of the calibration curve is such that the accuracy of measurement increases as the salinity diminishes. In addition to this scale convergence there is a milliammeter reading error of approximately $\pm 2$ per cent of the full scale deflection which arises in part from the error of the eye in reading the meter and in part from errors in the reproducibility of the pointer movement itself. These errors, together with those remaining after temperature compensation, are given in Fig. 40, which assumes the temperature error to be zero at $20^\circ C$.

Of the salinometers in use at present, this salinometer is less accurate and more sensitive to temperature than others. But it has the great advantage of portability, which, together with its simplicity, wide range and ease of calibration, makes it useful for programs of work where the salinity gradients are large and abrupt, or where it is desirable to measure the initial thickness and mixing zones of excessively thin layers of water. It is also inexpensive to build and maintain.

Mr. T. Wehe has earned the writer's gratitude for his painstaking assistance in making repeated thermal calibration runs and experiments with a large variety of electrode sizes and compositions.

SUMMARY

The salinometer is a simple electrical instrument for direct measurements in the field of a wide range of salinities. It is particularly well suited for use from a skiff, since it is light, portable and readily calibrated in the field. Because the approach is simpler, the instrument is described in terms of empirical relationships between the experimental variables rather than rigorously in terms of physical chemistry. From the experimentally derived curves the behavior of the instrument can be predicted sufficiently well for purposes of design and readaptation to special investigations.

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