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POTENTIOMETRIC ANALYSIS OF SEA WATER I. DETERMINATION OF CHLORINITY

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In general the determination of chlorinity of sea water is made by the classical Mohr method except when greater accuracy is desired in which case the more accurate but longer Volhard method is used. When the results are utilized for hydrodynamical considerations the Mohr method is normally used because of its speed in the titration of the numerous samples; but to attain the accuracy required in this exacting work, extreme care is demanded with the shaking during titration and in the proper selection of end point. A potentiometric determination seemed a convenient means of increasing the accuracy of the direct titration. For this purpose the apparatus recently described elsewhere by the authors (2) was used. It was found that the chlorinity could be determined potentiometrically with an accuracy and precision comparable to the Volhard (1) method in less time and with less labor than would be required by this latter method. As illustrative of the precision and accuracy of the potentiometric method, the following data are presented.

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SOLUTIONS

Silver Nitrate Solutions: Approximately 0.28 N AgNO_3 solution was preserved in a brown glass-stoppered bottle. Using a calibrated 25 ml. pycnometer its density was determined to be 1.03764 (in vacuo) at 20.0° C. A portion of the 0.28 N solution was diluted tenfold using calibrated volumetric apparatus.

Copenhagen Standard Sea Water: Two samples of standard sea water bottled at the Copenhagen Hydrographical Laboratories were used as standards. One was standardized in 1932 and had a chlorinity of 19.386‰ and the other in 1937 with a chlorinity of 19.393‰.

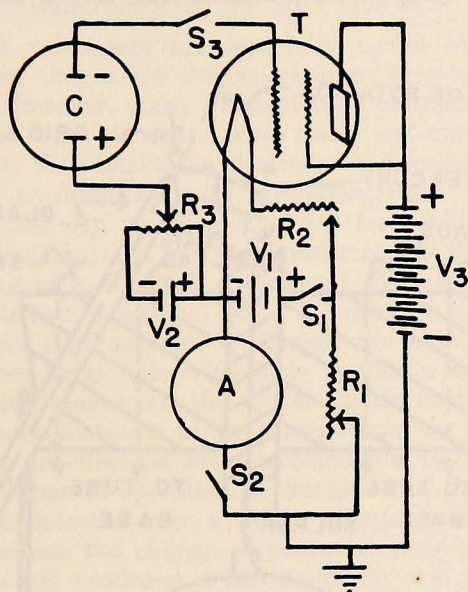
Standard Sodium Chloride Solution: A liter of solution contained 32.814 g. (in air) of purified and dried NaCl. Using a calibrated 25 ml. pycnometer its density (in vacuo) at 20° C. was determined to be 1.02110.

DESCRIPTION OF APPARATUS

The circuit diagram is shown in Figure 1. A Cunningham Radiotron vacuum tube, type 22, was selected because it seemed to have the most desirable characteristics (3) for the purpose at hand. The positive pole of the 2-volt battery V_2 was connected to the negative pole of the 4-volt battery V_1 thus allowing the 6-volt storage battery to serve a double purpose. As a precaution against drift and instability the vacuum tube and other parts easily affected by stray currents were inclosed in a copper screen-covered box, which was electrically grounded. Controls through a bakelite panel led into the box to operate the filament rheostat, a battery switch, the panel-type potentiometer and the control grid switch. The vacuum tube was placed inside the box in a stoppered glass cylinder in the bottom of which was placed a layer of desicchlora to maintain a dry atmosphere. The cylinder was closed with a rubber stopper through which passed the electrical leads from the tube socket terminals. The wire from the grid of the tube also passed through the stopper but was insulated from it by encasing in a $\frac{3}{8}$ " glass tube and filling with sulfur. The control grid switch was mounted on the rubber stopper as shown in Figure 2. The top part of the glass tubing which carried the grid lead through the stopper was used as a cup for the mercury grid switch. A glass rod which projected through the bakelite panel could be rotated to operate the switch. A flexible insulated wire on the shaft of the switch led out of the box to the titration cell. The length of the grid lead from the tube to the titration cell was less than six inches.

Tests with the apparatus showed its free grid potential to be

— 0.23 volts and its voltage sensitivity to be 3.2 millivolts per microampere. Although this voltage sensitivity was adequate for the determination of the end point of the chlorinity titration, an increased sensitivity of 1.25 m.v. per unit scale deflection resulted



C	Titration Cell
T	Vacuum tube, type 22
A	Microammeter (scale 0-300)
V ₁	4 volt storage "A" battery
V ₂	2 volt storage "C" battery
V ₃	45 volt dry "B" battery
R ₁	5000 ohms
R ₂	25 ohms
R ₃	10,000 ohm panel-type potentiometer
S ₁ , S ₂	Switches
S ₃	Control grid switch

Figure 1. Vacuum Tube Voltmeter.

by substituting a galvanometer (Leeds and Northrup No. 2320 D, current sensitivity 5×10^{-7} amperes) for the microammeter (Weston D.C. Microammeter Model 1). The maximum current flowing through the grid while operating near the free grid potential was found to be less than 3×10^{-11} amperes.

A motor-driven glass stirrer was mounted above the small titration beaker. The electrodes were conveniently fastened to, and

insulated from, the frame of the motor stirrer. The electrodes were connected so that the increasing negative pole was attached to the grid lead of the vacuum tube. Natural graphite with a surface area of 4 to 6 sq. cm. served as the reference electrode and a 4 to 6 inch piece of No. 20 tungsten or platinum wire served as the indicating electrode.

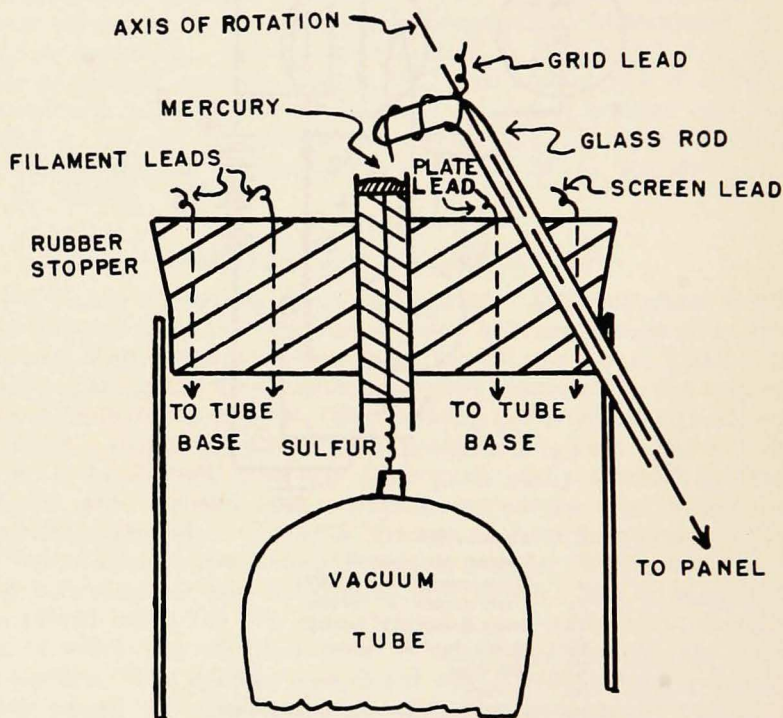


Figure 2. Control Grid Switch and Mounting.

OPERATION OF THE APPARATUS

S_1 , see Figure 1, was closed and switches, S_2 and S_3 , were left open. With the aid of a voltmeter, not shown in Figure 1, resistance R_2 was adjusted so that 3.3 volts was applied to the filament of the tube. Switch S_2 was then closed and by adjustment of R_1 the microammeter needle was set at a convenient value. The grid was then set at free grid potential by closing the switch S_3 and adjusting R_3 until the microammeter needle was again at its original setting. By

adjusting the grid to free grid potential before titration was begun and by connecting the electrodes in the manner indicated the grid was prevented from becoming positive during the course of the titration.

DISCUSSION OF APPARATUS

Vacuum tube voltmeters are especially useful in potentiometric titrations because they allow the course of a titration to be followed continuously. However, many vacuum tube voltmeters described in the literature are more elaborate, more costly and more sensitive than necessary for use with bimetallic electrodes in titrations of chlorinity. The apparatus as described here is characterized not only by its simplicity but also by its stability. Its free grid potential with respect to the negative end of the filament is less than 0.5 volt and at the beginning of a titration adjustment to this voltage is easily made in the manner described. The filament of the vacuum tube operates on only 0.13 ampere. Although the storage cells furnish a current of this magnitude with little fluctuation the same storage cells are used to balance out the initial steady portion of the plate circuit. Thus any fluctuation in the current from the filament battery is minimized in its effect on the microammeter in the plate circuit. Under the conditions of operation no fluctuation of the microammeter needle could be detected over a thirty minute period. During the course of a titration the change of potential between the electrodes of the titration cell produced a corresponding change in the microammeter reading which was recorded rather than the more familiar e.m.f. reading. The microammeter reading may be easily converted to volts by calibrating the instrument but such a conversion is unnecessary since any function proportional to the voltage is equally well suited for the determination of the end point. In general only a few seconds were required for the potential between the electrodes to reach a steady state except near the end point when about a minute was allowed. Usually the end point was determined from the microammeter readings by inspection. However it may be obtained graphically by plotting the change in microamperes per unit volume of titrant against the corresponding volume of titrant and is very well defined when obtained in this manner.

STANDARDIZATION OF SILVER NITRATE

Procedure: About 25 ml. of the standard sea water or the sodium chloride solution were weighed into a 100 ml. beaker which was covered with a watch glass during the weighings to prevent excessive

evaporation. The weighings were recorded to the nearest milligram. A volume of 0.28 N silver nitrate was added so that a slight excess of chloride-ion still remained. The silver nitrate was weighed to the nearest milligram. The beaker was placed in the titration position, the electrodes inserted into the solution and the mixture stirred for several minutes before the titration was continued. The titration was completed by adding the dilute silver nitrate solution from a micro buret. With vigorous stirring of the solution the electrodes usually reached a steady state within a few seconds after each addition of silver nitrate solution. The entire titration usually did not require more than five minutes for completion.

Experimental Data: Potentiometrically definite and appreciable changes in the microammeter readings were noted with the addition of as little as 0.01 ml. of the 0.028 N silver nitrate solution when near the end point. The data for a typical titration are recorded in Table I. These data are shown graphically in Figure 3.

Since about 50 ml. of 0.28 N silver nitration solution were used in the titration and the error of establishing the end point was not

TABLE I

DETERMINATION OF THE END POINT IN THE SILVER NITRATE STANDARDIZATION

<i>Mls. of Dilute AgNO₃</i>	<i>Plate Current Microamperes</i>	<i>Microamperes per 0.05 ml. AgNO₃</i>
0.00	100	
1.00	105	
1.85	114	
		1.0
1.90	115	
		1.0
1.95	116	
		2.5
2.00	118.5	
		3.0
2.05	121.5	
		4.0
2.10	125.5	
		3.0
2.15	128.5	
		2.5
2.20	131	
		1.0
2.25	132	

End Point = 2.07 ml.

more than 0.01 ml. of 0.028 N solution, an error of not more than 1 part in 50,000 could have resulted. This is a sensitivity hardly attainable by a visual colorimetric end point. Such a great sensitivity suggests that chlorinity could be determined on micro samples by this method with considerable accuracy.

In the particular determination for which the data in Table I were obtained, 51.381 g. (equivalent to 49.514 ml.) of the silver nitrate solution had been added to 25.531 g. of Copenhagen standard sea water ($\text{Cl} = 19.393\%$) before the titration was completed with the

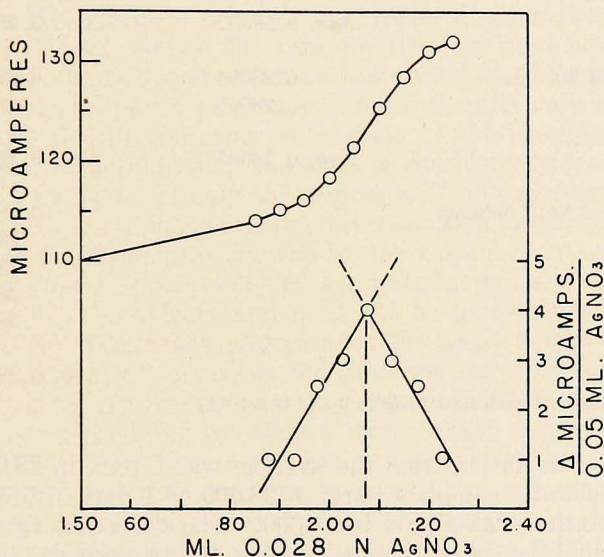


Figure 3. Titration of a Chloride Solution with Silver Nitrate.

dilute silver nitrate. The total volume of silver nitrate was then $49.514 + \frac{2.07}{10} = 49.721$ ml. Consequently the silver nitrate normality was $\frac{(25.531)(19.393)}{(49.721)(35.457)} = 0.28098$ with an error of not more than 1 part in 25,000 as far as the measurements were concerned. Results of other standardizations are shown in Table II. All weighings were corrected to in vacuo.

Discussion: These results listed in Table II are indicative of the precision that characterizes the potentiometric titration of chlorinity by the above method of determination. With one standard sea water

TABLE II

STANDARDIZATION OF SILVER NITRATE

<i>Standard Sea Water</i>	<i>Normality AgNO₃</i>	
	<i>Uncorrected for atomic weights</i>	<i>With new atomic weights*</i>
Cl = 19.386 ‰	0.28097	0.28112
	.28103	.28118
	.28096	.28111
	Ave. 0.28099	Ave. 0.28114
Cl = 19.393 ‰	0.28094	0.28109
	.28096	.28111
	Ave. 0.28095	Ave. 0.28110
<i>Standard NaCl Solution</i>		0.28119
		.28114
		.28112
		.28119
		.28115
	Ave. 0.28116	

*For recalculation with new atomic weights see (1).

the maximum deviation from the average was 1 part in 28,000, with the other sea water sample 4 parts in 28,000 or 1 part in 7,000. The average deviation was 1 part in 14,000. The difference between the average normalities as determined against the two sea water samples was 1 part in 7,000. Although this is a comparatively small variation it is somewhat greater than the experimental error of the determination. The accuracy of the potentiometric method as well as the Mohr and Volhard methods is limited largely by the amount of sorption of silver nitrate and sodium chloride by the silver chloride precipitate. With the Mohr method these occluded salts are brought into solution by manual shaking which at best is an indefinite and rather inefficient process. Moreover there is always some error in visual selection of the end point. With the Volhard method the excess silver nitrate is removed by washing of the silver chloride precipitate. Obviously only those salts on the surface are affected by the washing and those only partially since occluded salts can never be completely removed. Potentiometrically the salts need not be extracted but only brought to the surface to make them avail-

able for titration. Those salts within the silver chloride curds which are never exposed are not obtained by any method and so reduce the accuracy of the titration. It should be mentioned though that the mechanical stirrer is quite effective in the breaking of the silver chloride particles. Although the final accuracy of the determination may be more accurate than the standardization through a compensation of errors, it is desirable not to be dependent upon this stratagem whenever possible.

The potentiometric titrations may be made not only with great accuracy and precision but also with considerable rapidity. If the sample and silver nitrate solution are measured volumetrically as is done for the Mohr method the time for titration need not be much longer than would be required for the Mohr method while at the same time the accuracy would be greater. Since there is only one standard solution, no filtration and no washing of the precipitate in the potentiometric determination, the time is considerably less than for the Volhard method. If only the sample and the concentrated silver nitrate solution are weighed and the dilute solution measured volumetrically as is the procedure followed by the Copenhagen Laboratories in the preparation of the analyzed sea water samples, the weighings may be made very quickly and need not be particularly time consuming. If great accuracy is demanded the usual weight burets are essential but for most purposes the solutions may be weighed in a covered beaker. By making the weighings in the beaker, only three weighings are needed and by using a tared beaker and by measuring the sample and silver nitrate solution volumetrically into the beaker the approximate weights are already known and consequently little time is needed for final adjustment of the weights. A chainomatic balance is particularly appropriate for such routine weighings. Also by measuring and weighing the sample the approximate density and chlorinity of the water may be ascertained quickly so that the correct amount of the silver nitrate solutions may be added for weighing.

The titration of a sea water sample would be made in a manner identical to the above procedure for the standardization of the silver nitrate solution. Such titrations with this apparatus could be made aboard ship, particularly for titrations with only volumetric measurements of solutions. Obviously the use of a microammeter would make such titrations impractical on board ship in very rough seas. Consequently the greatest utility of the apparatus would be for very accurate work ashore.

The main disadvantage of course is that a special apparatus must be built and cannot be purchased as such. However the parts are either standard electrical equipment or may be purchased at radio

stores at a very small cost. The apparatus is relatively simple to construct and to operate.

SUMMARY

The results of potentiometric chlorinity titrations of sea water have been described using bimetallic electrodes and a vacuum tube voltmeter.

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