

YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



A PRECISE DETERMINATION OF CHLORINITY OF SEA WATER USING THE Ag-AgCl INDICATOR ELECTRODE

By

J. C. HINDMAN,¹ L. J. ANDERSON² AND E. G. MOBERG

*Scripps Institution of Oceanography
University of California
La Jolla, California*

A knowledge of the relative currents of the oceans depends to a large extent upon a knowledge of the distribution of mass. Measurements of temperature and chlorinity³ are made to furnish the necessary data for the computations of the density. The thermometers used are accurate to $\pm 0.02^\circ$ C. For an equal degree of accuracy, the chlorinity measurements should be made to ± 0.001 ‰ Cl. For routine work the Mohr titration with an accuracy of ± 0.01 ‰ Cl is used. This limit of accuracy is not important except for measurements where small chlorinity differences are significant (e. g., in the deep sea). A method suitable for the latter work, to replace the Volhard method used in the preparation of standard solutions, is desirable. Potentiometric titrations of halide are known to be highly precise (4). West and Robinson (7) applied such a method to the determination of chlorinity and reported a precision of better than $\pm 0.01\%$. These authors used bimetallic electrodes for their end-point indicators. While engaged in preparing secondary standard chloride solutions, we had occasion to use certain bimetallic electrode couples but were unable to obtain satisfactory results. As a consequence, further investigation of the method was undertaken and satisfactory results were obtained in using silver-silver chloride electrode in combination with an enclosed reference electrode. The data are presented herewith.

REAGENTS

Silver Nitrate: Two solutions of approximately 0.22N silver nitrate were stored in dark brown bottles. A weighed portion of each of these was diluted ten-fold in calibrated volumetric glassware.

¹ Present address: Argonne National Laboratory, Chicago, Illinois.

² Present address: U. S. Navy Electronics Laboratory, San Diego 52, California.

³ Chlorinity (‰ Cl) is defined as the weight in grams (*in vacuo*) of the halides contained in one kilogram of sea water (*in vacuo*) when all the bromides and iodides have been replaced by chlorides.

Copenhagen Standard Sea Water: Samples of the water bottled by the Hydrographic Laboratories of Copenhagen in 1937, and labeled with the chlorinity 19.393 ‰, were used as one set of standards. This water had been originally standardized against silver nitrate, prepared from atomic weight silver by the Volhard procedure (3), with a reported accuracy of $\pm 0.0005\%$.

Sodium Chloride: Merck blue label salt was recrystallized once from its saturated solution with HCl gas and once from a saturated solution with alcohol. The alcohol was purified by redistillation from alkaline silver nitrate. The salt was dried from four to eight hours in an electric furnace at the crackling temperature (500–600° C.) to remove the last traces of water.

Potassium Chromate Indicator: A saturated solution of K_2CrO_4 was prepared chloride free.

Water: Distilled water was redistilled from alkaline permanganate solution.

APPARATUS

The measuring component of the end-point indicator system was the direct reading vacuum-tube voltmeter developed by Anderson and Hindman (1).

Various combinations of the following metallic electrodes were investigated. Tungsten, chromium and gold electrodes were prepared by electrolysis of solutions of their salts using platinum foil anodes and cathodes. For the silver electrodes silver wires were employed. A graphite rod was used as the carbon electrode.

Silver-silver chloride electrodes were prepared from silver wire by electrolysis in 0.1 molar sodium chloride solution at a current density of 0.001 amp. per electrode. Care was taken to keep the layer of silver chloride as thin as possible. As a reference half-cell to be used with this electrode, a wick type electrode similar to the calomel electrode of ZoBell and Rittenberg (8) was entirely satisfactory. In this type of electrode, contact with the external solution is made through a small asbestos fiber sealed into the outer glass envelope. A platinum wire immersed in saturated potassium nitrate solution was used, however, in place of the internal calomel cell of the above authors. The electrode has numerous advantages; it is easily constructed, rugged and has had no perceptible contamination or solution leakage in several months of usage.

PROCEDURE

The titration procedure was essentially the same as that used by West and Robinson (7). For standardizations using the Copenhagen

water, a 15 ml sample was delivered from a pipette into a 100 ml beaker and weighed. A quantity of concentrated silver nitrate solution approximately 0.25 ‰ Cl (1.2%) less than equivalent to this amount of chloride was added rapidly from a burette and the beaker was again weighed. The solution was covered with a watch glass during the weighing to minimize evaporation. The beaker was then transferred to the titration assembly and mechanically agitated for several minutes, after which time the titration was completed by addition of the dilute silver nitrate from a microburette. The precision of the end-point was ± 0.01 ml, corresponding to a maximum error of approximately $\pm 0.0005\%$.

For the check standardizations, dry sodium chloride was weighed out, dissolved in about 25 ml of water, the silver nitrate added, and the titrations completed as described above. All weights were corrected to vacuo.

RESULTS

It was found, in general, that none of the bimetallic couples tested gave satisfactory results. While a break could be observed at first at the end-point of the titration, after a few minutes the electrodes tended to become passive. In every case it was noted that the electrode surfaces were discolored, probably from a coat of silver chloride. A similar explanation has been offered by Van Name and Fenwick (6) for the behavior of ignited platinum electrodes in titrations of silver nitrate with sodium chloride. The bimetallic electrodes used by us also suffered from another disadvantage, namely, that their potential changes were never as large as those observed when reversible electrodes were used. The actual potential changes were approximately one-tenth as large when the bimetallic electrodes were employed as when a silver-silver chloride indicator electrode was used. Since the silver-silver chloride and reference electrodes are easy to prepare, there is no advantage in using irreversible systems. The silver-silver chloride electrodes do become sluggish after considerable use. This is due to a gradual thickening of the layer of the salt on the surface of the electrode. If the surfaces are wiped with a clean cloth before putting the electrodes away after work, they may be preserved more or less indefinitely. Silver electrodes are also satisfactory but slightly more erratic in behavior than those of silver-silver chloride.

The results of the potentiometric standardizations of the silver nitrate solutions with the Copenhagen water and sodium chloride are shown in Table I. In computing the chloride equivalence of Copenhagen water it is necessary to correct for the difference in atomic weights between the present values and those of the original (1902)

TABLE I.—STANDARDIZATION OF SILVER NITRATE

<i>Copenhagen Water</i>	<i>Sodium Chloride</i>	<i>Copenhagen Water</i>	<i>Sodium Chloride</i>
<i>Silver Nitrate No. 1</i>		<i>Silver Nitrate No. 2</i>	
<i>mgm. Cl per gm.</i>	<i>AgNO₃ solution</i>	<i>mgm. Cl per gm.</i>	<i>AgNO₃ solution</i>
7.4712	7.4710	7.4658	7.4665
7.4701	7.4724	7.4658	7.4653
7.4721	7.4705	7.4655	7.4652
7.4712		7.4652	
7.4710			
Average 7.4711	7.4713	7.4656	7.4657
Av. deviation \pm .0005	\pm .0007	\pm .0002	\pm .0006

potassium chloride standard which furnishes the unvarying reference value for chlorinity determination. The chloride equivalent is 1.00045% Cl (3). The maximum average deviation from the mean of the checks is $\pm 0.009\%$. The best results, using the potentiometric method, reported in the literature are those of Lange and Schwartz (4) who were able to obtain a precision of about $\pm 0.003\%$. The agreement between the Copenhagen water and sodium chloride standardizations was excellent, confirming the findings of Thompson (5) that secondary standard waters may be prepared using sodium chloride as primary standard.

Table II indicates comparative data on the modified potentiometric and Mohr methods. In this case weight procedures as outlined above were used for both indicators. The results show that the precision of the two methods is about the same. It is probable that the difference in chlorinity found by the two methods can be ascribed to an absolute error in determining the true end-point by the Mohr procedure.

Investigations were also made of the degree of precision obtainable when the potentiometric method was used in routine chlorinity determination. Table III shows the results of a series of determinations made in quadruplicate. The potentiometric results were obtained by us. The comparison results were obtained by trained technicians following the routine procedure used in this laboratory. This procedure differs from that described by Helland-Hansen (2) in that mechanical stirring is employed. The precision is greatly improved by this departure. The potentiometric procedure was identical with the exception of the end-point indicator. The results show that the deviations in check runs are smaller by the potentiometric method. However, other sources of error, such as temperature changes, burette

and pipette drainage effects, are sufficient to make the accuracy of the determinations about the same for both methods. Where high accuracy is desired, and where precautions are taken to minimize these sources of error, the potentiometric end-point indicator is found to give considerably more reliable results.

TABLE II.—PRECISE CHLORINITY DETERMINATIONS BY THE MOHR AND POTENTIOMETRIC METHODS

<i>Sea Water</i>	<i>%₀₀ Cl potentiometric</i>	<i>Average deviation from mean</i>	<i>%₀₀ Cl Mohr</i>	<i>Average deviation from mean</i>
No. 3	18.426		18.422	
	18.429		18.418	
	18.426		18.420	
	Av. 18.427	±0.0013	18.420	±0.0013
No. 27	19.016		19.010	
	19.015		19.012	
	Av. 19.015	±0.0005	19.011	±0.001

TABLE III.—ROUTINE VOLUMETRIC DETERMINATION OF CHLORINITY

<i>Depth (m)</i>	<i>Mohr Chlorinities</i>			<i>Potentiometric Chlorinities</i>		
	<i>1st</i>	<i>2nd</i>	<i>Av.</i>	<i>1st</i>	<i>2nd</i>	<i>Av.</i>
0	18.475	18.470	18.473	18.486	18.486	18.486
10	18.470	18.475	18.473	18.497	18.495	18.496
20	18.405	18.400	18.403	18.400	18.402	18.401
30	18.360	18.360	18.360	18.366	18.365	18.366
40	18.310	18.320	18.315	18.317	18.317	18.317
50	18.310	18.320	18.315	18.317	18.314	18.316
75	18.465	18.475	18.470	18.472	18.475	18.474
100	18.555	18.550	18.553	18.549	18.550	18.550
150	18.745	18.730	18.738	18.751	18.753	18.752
200	18.850	18.840	18.845	18.854	18.853	18.854
250	18.880	18.880	18.880	18.895	18.895	18.895
300	18.945	18.935	18.940	18.954	18.954	18.954
400	18.960	18.960	18.960	18.978	18.975	18.977
500	18.980	18.975	18.978	18.999	19.001	19.000
600	19.005	18.995	19.000	19.022	19.022	19.022
Average diff. between duplicates			0.007			0.0015

SUMMARY AND CONCLUSIONS

A potentiometric method for precise chlorinity determinations is described. Standardization of two silver nitrate solutions, using Copenhagen water as a secondary standard as well as pure sodium chloride as a primary standard, gave results agreeing to $\pm .002\%$ with a probable error of $\pm .007\%$. The suitability of sodium chloride as a primary standard in the preparation of secondary standard sea waters is thus confirmed.

When the method was used to determine the chlorinity of sea water, a probable error of $\pm .005\%$ is obtained. Used in the routine titration of sea water, a probable error of $\pm .008\%$ is obtained as compared to $\pm .040\%$ for the standard Mohr titration procedure.

Certain bimetallic electrodes were found to be inferior in performance and reliability to the reversible silver-silver chloride electrode.

REFERENCES

1. ANDERSON, L. J. WITH J. C. HINDMAN
1943. A versatile continuous reading thermionic voltmeter. *Industr. Engng. Chem., Anal. Ed.*, 15 (1): 42-45.
2. HELLAND-HANSEN, BJÖRN
1912. The ocean waters, an introduction to physical oceanography. I. General Part (Methods). III. Salinity. *Int. Rev. Hydrobiol., Hydrogr. Suppl., Ser. 1*: 30-47.
3. JACOBSEN, J. P. AND MARTIN KNUDSEN
1940. Urnormal 1937 or primary standard sea water 1937. *Publ. sci. Ass. Océanogr. phys.*, 7: 1-38.
4. LANGE, E. AND E. SCHWARTZ
1927. De Potentialkurve bei potentiometrischen Fällungstitationen. *Z. phys. Chem.*, 129: 111-127.
5. THOMPSON, T. G.
1928. The standardization of silver nitrate solutions used in chemical studies of sea waters. *J. Amer. chem. Soc.*, 50: 681-685.
6. VAN NAME, R. G. AND F. FENWICK
1925. The behavior of electrodes of platinum and platinum alloys in electro-metric analysis. *J. Amer. chem. Soc.*, 47: 9-29.
7. WEST, L. E. AND R. J. ROBINSON
1941. Potentiometric analysis of sea water. I. Determination of chlorinity. *J. Mar. Res.*, 4 (1): 1-27.
8. ZOBELL, C. E. AND S. C. RITTENBERG
1937. An asbestos KCl bridge and a simple calomel electrode. *Science*, 86: 502.