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INTERNATIONAL FISHERIES COMMISSION**

APPOINTED UNDER THE TREATY BETWEEN  
THE UNITED STATES AND GREAT BRITAIN FOR THE  
PRESERVATION OF THE NORTHERN PACIFIC  
HALIBUT FISHERY

NUMBER 3.

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**DETERMINATION OF THE CHLORINITY  
OF OCEAN WATERS**

*by*

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## FOREWORD

The present is a third report by the International Fisheries Commission upon scientific results obtained under the terms of the Convention of 1924 between the United States and Great Britain for the preservation of the halibut fishery of the Northern Pacific Ocean, including Bering Sea.

It describes certain of the chemical methods used in obtaining the data dealt with in Report Number 4, by George F. McEwen, Thomas G. Thompson and Richard Van Cleve, which is a technical study of the rate and direction of those currents which affect the distribution of the eggs and larvae of the halibut in the Gulf of Alaska.

The International Fisheries Commission has had the help of an advisory board of four members: Dr. C. McLean Fraser, Dr. W. A. Clemens, Mr. N. B. Scofield, and the late Prof. John N. Cobb.

The investigations have been carried on by a staff under the direction of William F. Thompson, with headquarters and laboratory at the University of Washington, Seattle, U. S. A.

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## REPORTS BY THE INTERNATIONAL FISHERIES COMMISSION

1. Report of the International Fisheries Commission appointed under the Northern Pacific Halibut Treaty, by John Pease Babcock, Chairman, and Wm. A. Found, Miller Freeman, and Henry O'Malley, commissioners. Dominion of Canada, Ottawa, 1928.  
Same. Report of the British Columbia Commissioner of Fisheries for 1928, pp. 58-76. Victoria, 1929.  
Same. Report of United States Commissioner of Fisheries for 1930, Appendix 1. U. S. Bureau of Fisheries Document No. 1073. Washington, 1930.
2. Life History of the Pacific Halibut (1) Marking Experiments, by William F. Thompson and William C. Herrington. In press.
3. Determination of the Chlorinity of Ocean Waters, by Thomas G. Thompson and Richard Van Cleve.

Further reports will bear serial numbers and will be issued separately by the commission.



## DETERMINATION OF THE CHLORINITY OF OCEAN WATERS

THOMAS G. THOMPSON AND RICHARD VAN CLEVE

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### INTRODUCTION

The application of the method of Mohr (1856) to the determination of the chlorinity<sup>1</sup> of sea water, using potassium chromate as an indicator, has been generally adopted for oceanographical investigations as a means for the calculation of densities *in situ* when the temperatures are known. The accuracy of Mohr's method has been demonstrated or favorably discussed by a number of investigators,<sup>2</sup> while its applicability to various changes of *pH* has been shown by Doughty (1924) and van Urk (1925). On the other hand, its accuracy for the calculation of densities from titration values and the Hydrographical Tables (Knudsen, 1901) has been questioned by several California workers (Michael and McEwen, 1915; Miller, Ramage, and Lazier, 1928), and by Sewell (1928). Michael and McEwen (1915) on 46 determinations, using the titration method and a pycnometer, obtained an average variation of 0.00006 for density, with a maximum plus and minus variation of 0.00017. The observations of Michael and McEwen (1915) are very much in accord with unpublished data of one of the authors. On surface samples taken at hourly intervals over a period of 25 hours, and using a 50 ml. pycnometer, T. G. Thompson found that an average deviation between calculated and observed values of 0.00004 was obtained at 15° C. The maximum minus variation of 0.00005, while 0.00018 was the maximum plus variation. Such discrepancies have been attributed by Sewell (1928) to changes in the components of the sea water. In support of this statement the interesting work of Matthews (1916-17) and of Atkins (1926) and Harvey (1926, 1928) and Atkins and Harvey (1926) may be cited. They have shown that marked changes in the concentrations of phosphates, silicates, and nitrates took place as the result of metabolic activity of various organisms. However, these substances occurred in quantities that were measurable only as milligrams per cubic meter of water, and such changes as observed would have

<sup>1</sup>The chlorinity is defined as the number of grams of chlorine contained in one kilogram of sea water, assuming the small quantities of bromine and iodine are replaced by chlorine.

<sup>2</sup>Knudsen (1902, 1903, 1925); Bjerrum (1904); Ruppin (1910); Helland-Hansen (1912); Manuelli (1914); Bjerkkan (1919); Matthews (1926); Smith and Thompson (1927); and Thompson (1928).

had only a very minute effect upon the densities of the waters. Gran (1928), Hutchinson (1927), Moberg (1928), and Sewell (1928) have shown the effect of phytoplankton in altering the composition of coastal waters, and Hitchings, Todd, and Thompson (1928) found variations in the concentration of the bicarbonate ions where the rate of photosynthesis was very marked. However, it must be emphasized that many of these variations are very small indeed in respect to the entire mass of water, and that when they do occur, are most pronounced near the surface and in estuaries.

Pettersson (1883), Hamberg (1886), and Ringer (1906) have demonstrated that, in proportion, more of the sulfate than of the chloride ions are retained by the sea ice in its formation. The sulfate-chloride ratio of the waters under the ice varied from that of regular sea water, as did that of the water resulting from the melting of the ice. Thompson, Lang, and Anderson (1927) have demonstrated that natural dilution has a tendency to alter the constancy of the sulfate-chloride ratio but that in general the ratio is decidedly constant. Variations in the constancy of the calcium and magnesium ions in respect to one another and to the chlorinity have been demonstrated by Bertrand, Freundler, and Ménager (1922), and Giral (1924, 1926), while Matthews and Ellis (1928), and Thompson and Wright (1930) have shown constant relationships for these ions. The latter attribute the variations obtained by other workers to errors in the procedures recently pointed out by Epperson (1928), and to improper separations.

Changes in the concentrations of dissolved gases in different water strata are well known to occur. These changes will produce a greater difference between a direct density determination and a calculated value than some of the factors described above. Water that is stored for periods of time before direct density determinations<sup>1</sup> are made have a tendency to either liberate or absorb gases, especially when exposed to atmosphere during the transfer from one vessel to another.

The authors have noted decided changes in the silicate content of water on storage for short periods of time, particularly with the so-called citrate bottles. The silicate content varied in some cases from 1.5 mg. per liter to 6 and 8 mg. when well-seasoned bottles were used. With unseasoned bottles an increase to 22 mg. of silica was noted within a week.

Such errors as cited above affect direct density determinations. Failure to maintain exact conditions of temperature is an outstanding source of error.

After a study of the literature, supported by considerable laboratory experience, it has been concluded that the best means of ascertaining the most probable density is by the determination of the chlorinity and the use of the Hydrographical Tables.

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<sup>1</sup>In referring to direct density determinations the authors have in mind only the pycnometer method and the method of McEwen (1915), for they feel that the use of the hydrometer was ruled out of oceanographical investigations years ago.

## EXPERIMENTS

In the investigations of the waters of the northeast Pacific, three different modifications of Mohr's method have been used. The chief differences were in the amount of sample taken and the concentration of the silver nitrate solutions used for titrations. Questions have been raised at times as to the comparability of results obtained by such procedures. Accordingly it was decided to make a study of the different modifications, using them in much the same manner employed in actual practice, and to compare them with the gravimetric method and Volhard's volumetric process.

The three modifications of Mohr's method are:

1. The employment of the special Knudsen pipet and buret using the normal water of the Hydrographic Laboratories of Copenhagen (Knudsen, 1903, 1925) for standardization of the silver nitrate solution.

2. The use of ordinary volumetric apparatus made to meet the specifications of the United States Bureau of Standards, the use of 25 ml. of sea water for titration and solutions of silver nitrate equivalent to 10 mg. of chlorine per liter. The latter may be standardized with solutions of sodium chloride or with the normal water of the Hydrographic Laboratories. The parts per mille are calculated from the chlorinity per liter at 20° from the following formula, where  $Cl_v$  is the chlorinity per liter and  $Cl_w$  the chlorinity per kilogram (Thompson, 1928).

$$Cl_w = 0.008 + 0.99980 Cl_v - 0.001228 Cl_v^2.$$

Table 1 gives the correction necessary for converting chlorinity per liter to chlorinity per kilogram as calculated from the above formula.

3. The use of ordinary calibrated volumetric apparatus, 5 ml. samples of sea water, and silver nitrate solutions approximating 0.1 *N* standardized against sodium chloride. In some respects it is to be regretted that such results are reported on a volume basis rather than that of weight.

The employment of sodium chloride solutions, suggested by Ménager (1924) and Giral (1926) and elaborated by Thompson (1928), have always given, in this laboratory, practically the same values to the silver nitrate solutions that are obtained by the use of the normal water supplied by the Hydrographic Laboratories. Standard solutions of sodium chloride and ordinary volumetric apparatus have proved to be of considerable convenience at times, as both may be procured on very short notice. The only objection to this method is that the results are obtained on a volume basis, but these may be readily converted to parts per mille by substituting in the above formula or applying the corrections given in Table 1. Thus to convert chlorinity per liter to chlorinity per kilogram, the necessary correction is ascertained from Table 1 and subtracted from the chlorinity per liter.

In Table 2 are given the results of the analyses of nine composite samples of sea water prepared from various samples taken at different depths and stations in the Gulf of Alaska.

The second column of the table shows the results of the gravimetric method. The data were secured by pipetting into a beaker 25 ml. of the filtered sea water, acidifying with nitric acid, diluting with 50 ml. of water, and precipitating the silver halides by adding an excess of silver nitrate. After boiling to coagulate the precipitate, and then cooling, the silver halides were collected on an asbestos filter, washed and dried to constant weight. The silver halides were corrected so that the silver bromide was calculated as the chloride.

The third column of the table gives the results obtained by using Volhard's method as outlined by Smith (1922), using 25 ml. samples, 0.2500 *N* silver nitrate, and 0.0502 *N* ammonium thiocyanate.

In the fourth column are shown the data obtained by the use of the Knudsen pipet and buret and following the procedure of the Hydrographic Laboratories. The Knudsen buret used in this study was not the later bulb type buret, and the readings were thus probably not as accurate as those obtained with the ordinary apparatus or if the bulb type had been used.

The data in the fifth column were secured by the use of ordinary calibrated apparatus and 25 ml. of sea water as outlined above.

The sixth column contains the data obtained by the use of 5 ml. sea water and a more dilute solution of silver nitrate. This particular procedure has been used and described by Miller, Ramage and Lazier (1928), and by Lucas (1927) and Hutchinson (1927). The latter claim an accuracy of 3 parts in 2000, or 0.015 per mille.

The data given in the last three columns of the table are the averages of independent series of analyses of the same waters by both of the authors. With the Knudsen apparatus the greatest variation between observers was 0.04 per mille, and this was obtained on three of the samples. This variation was undoubtedly produced by the rapid delivery of the buret and resultant error of drainage. With the second modification of Mohr's method, the greatest variation was 0.02 per mille, while the third modification, using 5 ml. of water, gave differences of 0.04 per mille in one case and 0.05 per mille in another, but otherwise the accuracy was in accord with the statement of Lucas and Hutchinson. For the total of 27 analyses, representing the three modifications of Mohr's procedure, the following variations between the two observers were obtained:

Exact checks	8
Within 0.01 per mille	7
Within 0.02 per mille	6
Within 0.03 per mille	1
Within 0.04 per mille	4
Within 0.05 per mille	1

The above show an average error of 0.016 per mille with waters having a chlorinity from 17.86 per mille to 18.97 per mille. Omitting the results secured with the older type of Knudsen buret, the error is reduced to 0.013 per mille, which is in accordance with that reported by Oxner and Knudsen (1920).



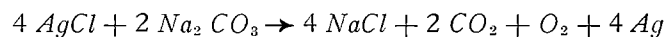
The main sources of error in Mohr's method may be summarized as follows:

(a) Failure to thoroughly stir or mix the solution during the process of titration in order to break up the curds of silver chloride.

(b) The addition of insufficient quantities of the indicator. Three drops of the saturated solution of potassium chromate is sufficient to give a concentration so that the solubility product will be exceeded when just a portion of a drop of silver nitrate solution is added in excess. The end point correction is so small that it can be neglected.

(c) Use of apparatus that fails to meet the specifications of the United States Bureau of Standards or the Hydrographic Laboratories.

The main objection to the chlorinity method is the cost of silver nitrate. This is not a serious objection as the material may be readily and easily reclaimed. After experimenting with the different methods for the recovery of silver, the following is the one recommended: The silver residues are dried and then mixed with about 25 per cent more than the theoretical amount of crude anhydrous sodium carbonate.



The mixture is placed in a Hessian crucible and the latter set in an ordinary pot furnace heated by a large blast lamp. As the material reacts and melts, more of the mixture is added. The molten mass is finally poured into a suitable mould and on cooling the silver is readily separated from the slag. This silver is then remelted in the presence of powdered charcoal and poured as a fine stream into a large bucket of cold water. Silver flakes or shot are thus produced that are free from occluded sodium chloride, and after washing with water are dissolved in nitric acid. The resulting solution is evaporated to dryness to remove excess acid. This is essential, otherwise it would be impossible to use a solution of the salt for titration, as the excess hydrogen ions from the nitric acid would prevent the formation of the silver chromate and thus obscure the end point.

## SUMMARY

1. An outline of the literature dealing with factors that may produce possible variations between the calculated and determined densities, is given.

2. Modifications of Mohr's method, which differ as to type of volumetric apparatus used, size of sample and concentration of silver nitrate solution, all give practically the same results.

3. Errors in direct density determinations were found to result from permitting an elapse of time between collection and analysis of the samples.

4. In the authors' opinion, the determination of chlorinity gives the best method for the calculation of the most probable density *in situ* at atmospheric pressure.

TABLE 1.—Corrections for converting chlorinity per liter to chlorinity per kilo at 20°C.

Cl per Liter	Correction	Cl per Liter	Correction
9.95 — 10.35	-0.12	15.88 — 16.17	-0.31
10.36 — 10.75	-0.13	16.18 — 16.32	-0.32
10.76 — 11.15	-0.14	16.33 — 16.62	-0.33
11.16 — 11.46	-0.15	16.63 — 16.82	-0.34
11.47 — 11.76	-0.16	16.83 — 17.11	-0.35
11.77 — 12.06	-0.17	17.12 — 17.32	-0.36
12.07 — 12.46	-0.18	17.33 — 17.57	-0.37
12.47 — 12.86	-0.19	17.58 — 17.82	-0.38
12.87 — 13.07	-0.20	17.83 — 18.02	-0.39
13.08 — 13.37	-0.21	18.03 — 18.27	-0.40
13.38 — 13.67	-0.22	18.28 — 18.47	-0.41
13.68 — 14.02	-0.23	18.48 — 18.67	-0.42
14.03 — 14.27	-0.24	18.68 — 18.97	-0.43
14.28 — 14.52	-0.25	18.98 — 19.17	-0.44
14.53 — 14.62	-0.26	19.18 — 19.32	-0.45
14.83 — 15.09	-0.27	19.33 — 19.52	-0.46
15.10 — 15.37	-0.28	19.53 — 19.77	-0.47
15.38 — 15.68	-0.29	19.78 — 19.97	-0.48
15.69 — 15.87	-0.30		

TABLE 2.—Analysis of nine samples of sea water by various methods and modifications.

Sample No.	Gravimetric Method o/oo Cl	Volhard's Method o/oo Cl	Mohr's Method		
			A o/oo Cl	B o/oo Cl	C o/oo Cl
1	17.86	17.85	17.86	17.86	17.85
2	17.99	17.99	17.96	17.99	18.03
3	18.00	18.02	18.00	18.02	18.02
4	18.74	18.73	18.76	18.73	18.76
5	18.79	18.78	18.79	18.79	18.78
6	18.82	18.81	18.78	18.81	18.78
7	18.92	18.91	18.92	18.93	18.92
8	18.94	18.94	18.92	18.94	18.93
9	18.97	18.96	18.97	18.96	18.98
Average	18.559	18.554	18.551	18.559	18.561

A, B, and C are modifications of the Mohr method and the results are the mean of independent determinations of the two authors. A, method of Knudsen; B, method of Thompson; C, method described by Miller et al and Lucas and Hutchinson with results converted to chlorinity per kilo.

Corrections were made in the gravimetric method so that the small amount of the silver bromide was calculated as silver chloride.

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