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THE POTASSIUM-CHLORINITY RATIO
OF OCEAN WATER

By

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ABSTRACT

A method for determining the amount of potassium in ocean water has been described. With this procedure, a number of ocean water samples have been analyzed for potassium, and the potassium-chlorinity ratios have been calculated. The ratio has been found to have a constant value of 0.02023 with a standard deviation of 0.000,032 or 1.6 parts per 1,000.

INTRODUCTION

Ocean water is a complex solution of many ions, among which the chloride ion is predominant. It has been shown that the relative concentrations of the major ions bear a surprisingly constant ratio to one another even though the total concentrations of ions vary from place to place in the oceans. In Table I the ion-chlorinity ratios of some of the major ions in sea water are tabulated for comparative purposes. The potassium-chlorinity ratio is not listed because of the variability of previous results which probably resulted from difficulties of analysis for potassium.

In Table II are summarized the estimates of the potassium-chlorinity ratio based upon the analyses of various investigators since 1880. These results are subject to criticism because of uncertainties in the methods of analysis, use of erroneous atomic weights, lack of correction for air buoyancy in weighing and use of an improper reference standard for chlorinity. It appears that Dittmar's ratio for potassium carries the most weight among these values because his early work on the composition of sea water in general has proven to be quite reliable and is an accepted reference where more recent work is in doubt. Lyman and Fleming (4) also arrived at a value of 0.02029 for Dittmar's ratio after correcting for air buoyancy in weighing, for the reference standard used for chlorinity and for changes in atomic weights.

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TABLE I. THE ION-CHLORINITY RATIOS OF SOME OF THE
MAJOR IONS IN OCEAN WATER

Ion	Chlorinity Ratio	Precision[a] (°/oo)	Authority
Sodium	0.5556	2	Robinson and Knapman (7)
Sulfate	0.1394[b]	2.4	Thompson *et al.* (10)
Magnesium	0.06695[b]	1.6	Thompson and Wright (11)
Calcium	0.02150	2.9	Thompson and Wright (11)

[a] These values are the standard deviations of the results published in the literature.

[b] These values have been corrected for air buoyancy in weighing, for the reference standard used for chlorinity, and for changes in atomic weights as specified by Wichers (14).

TABLE II. PREVIOUS VALUES FOR THE POTASSIUM-CHLORINITY RATIO
OF OCEAN WATER*

Author	No. of Samples	Location	K/Cl[†]
Schmelck (1882)	6	N. Atlantic	0.02026[‡]
Forsberg (1883)	4	Siberian	.0211[‡]
Dittmar (1884)	77	All oceans, except Polar	.02029[‡]
Natterer (1892–4)	57	Mediterranean	.02008[‡]
Kolotoff (1893)	1	Black Sea	.0210[‡]
Makin (1898)	22[α]	Atlantic	.02036[‡]
Macallum (1903)	3	Atlantic	.02025[‡]
Schloesing (1906)	3	Atlantic, Mediterranean	.01953[‡]
Wheeler (1910)	5	Atlantic	.0263[‡]
Steiger (1910)	1	Atlantic	.01988[‡]
Anderson and Thompson (1929)	12	Puget Sound	.0191[‡]
Webb (1939)	1	Atlantic	.02009
Miyake (1939)	1[α]	Pacific	.0191

* Compiled chiefly by Webb (13).

† In most cases in which the method is described, the potassium was precipitated as chloroplatinate and was weighed either as such or more usually converted to platinum. Exceptions are the method of Webb, in which potassium silver cobaltinitrite was precipitated and titrated, and the method of Anderson and Thompson, in which potassium perchlorate was precipitated and weighed.

‡ Calculated by Webb (13) from the published analyses. The results of Dittmar and of Makin were corrected for changes in atomic weights. Natterer's ratios were corrected by reckoning bromide as chloride as in all other analyses.

[α] All the samples were pooled together to make one composite sample.

The present study arose from a desire to establish the potassium-chlorinity ratio with certainty. The analyses for potassium were performed by the method of Jentoft and Robinson (2), in which the potassium is precipitated as the metaperiodate and then estimated iodimetrically. This method is a modification of that originally reported by Willard and Boyle (15).

PROCEDURES

The chlorinities of the various ocean water samples were determined by the well known Mohr procedure as adapted to oceanographic analyses.
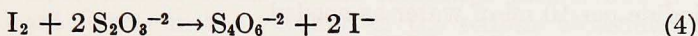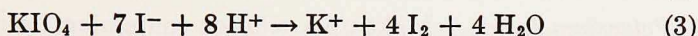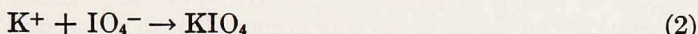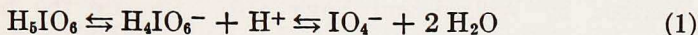
The theoretical considerations involved in the iodimetric determination of potassium as the metaperiodate have been discussed elsewhere by Jentoft and Robinson (2). The procedure for the analysis of potassium used in the present investigation is as follows:

Measure 25 ml sea water sample into a 100 ml beaker. Then add 0.2 ml of a 0.1% gelatin solution and 1.0 g of solid sodium cobalt-initrite and stir the solution until the sodium cobaltinitrite has dissolved. Cool the solution to about 0° C in an ice-bath, add 25 ml of 95% ethyl alcohol and refrigerate the solution at 0° C for eight hours. Filter the solution through a Gooch crucible and wash the precipitate and beaker once with 95% ethyl alcohol cooled to 0° C. Evaporate the alcohol completely on the steam bath and then dissolve the precipitate in 10 ml of hot 5 N nitric acid. (*Failure to evaporate the alcohol completely may result in an explosion when the nitric acid is added and heated.*) Next render the cobaltous ion inactive by precipitating with 10 ml of oxalic acid reagent. Then evaporate the solution to dryness on the steam bath.

Add exactly 2 ml of water to the dry sample to dissolve the potassium and then precipitate slowly with two 0.5 ml portions of periodic acid, spaced 10 minutes apart. Stir the solution occasionally after adding the reagent. Ten minutes later add 0.4 ml of lithium acetate solution, with rapid stirring, at the rate of about one drop (0.02 ml) per second. After 10 minutes add the lithium acetate reagent as before until the added 2, 6-dinitrophenol indicator turns dark yellow in color, indicating a pH of 3.0 to 3.5. Usually about 0.6 ml of lithium acetate is required in the second addition. Add two ml of 95% ethyl alcohol to the solution and cool the precipitate and solution with frequent agitation for 30 to 45 minutes in an ice-bath. Then decant the solution through a previously cooled 10 ml Gooch crucible prepared with a single-layer asbestos mat. Wash the precipitate with a 2-1 ethyl alcohol-isopropyl alcohol wash liquor also cooled to 0° C; the beaker

should be washed 4 to 5 times and the crucible 5 to 7 times, depending upon the amount of solids present.

Dissolve the potassium metaperiodate in 10 ml of 4 N sulfuric acid diluted with 25 ml of water. Add solution containing 1 g of potassium iodide and titrate the liberated iodine with standard sodium thiosulfate solution, using starch as the indicator. The equivalents of potassium are equal to one-eighth the equivalents of sodium thiosulfates used. The reactions involved are

$$H_5IO_6 \leftrightarrows H_4IO_6^- + H^+ \leftrightarrows IO_4^- + 2\,H_2O \tag{1}$$

$$K^+ + IO_4^- \rightarrow KIO_4 \tag{2}$$

$$KIO_4 + 7\,I^- + 8\,H^+ \rightarrow K^+ + 4\,I_2 + 4\,H_2O \tag{3}$$

$$I_2 + 2\,S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2\,I^- \tag{4}$$

REAGENTS AND SOLUTIONS

Reagent grade chemicals were used throughout this investigation unless otherwise stated.

Ammonium Molybdate. Prepare 3% ammonium molybdate solution to catalyze the reaction between bromate and iodide in acid solution according to the recommendation of Kolthoff and Sandell (3 p. 594).

Asbestos. Digest a good grade of asbestos with concentrated nitric acid for four hours, filter and wash with distilled water. This treatment is necessary to prevent retention of periodic acid which could not otherwise be washed free of the asbestos, causing high results.

2,6-Dinitrophenol. Prepare a 0.1% solution of 2,6-dinitrophenol by dissolving in water with the aid of an equivalent amount of lithium carbonate.

Gelatin. Prepare a 0.1% gelatin solution by dissolving granular gelatin in water saturated with mercuric iodide which will serve as a preservative.

Lithium Acetate. Prepare a 2.5 N lithium acetate solution by dissolving 18.5 g of purified lithium carbonate in 30 ml of glacial acetic acid and diluting to 200 ml.

The lithium carbonate was purified by double crystallization. Lithium carbonate was suspended in water and dissolved in a stream of carbon dioxide. The solution was filtered and the lithium carbonate was reprecipitated by heating the solution to the boiling point until evolution of the carbon dioxide was complete. After the second crystallization the lithium carbonate was dried at 120° C for 24 hours.

Organic Solvents. Redistill the ethyl and isopropyl alcohols before using, retaining those fractions which distill within a range of 1 to 3° C. Prepare a 2–1 ethyl alcohol-isopropyl alcohol wash liquor from these.

Oxalic Acid. Prepare a solution to contain 10 g of oxalic acid dihydrate per liter.

Periodic Acid. The periodic acid, obtained from the G. F. Smith Chemical Company, was found to be free of iodic acid by the test described by Willard and Boyle (15). Prepare the periodic acid reagent so that it contains 0.5 g of H_5IO_6 per ml. Since this solution deteriorates on standing, it was prepared fresh as needed.

Potassium Iodide. Make up a solution containing 1 g of potassium iodide per 10 ml of water as needed.

Potassium Iodate. Purify the potassium iodate by recrystallization and dry at 180° C to constant weight according to Scott (8, p. 1209). Prepare a 0.075 N solution on which to standardize the sodium thiosulfate solution.

A similar standard solution of potassium bromate was prepared according to Kolthoff and Sandell (3, p. 594).

Sodium Chloride. Recrystallize the sodium chloride from a saturated solution by precipitating with hydrogen chloride gas. After filtration and washing with distilled water, dry at 390° C for 12 hours.

Sodium Thiosulfate. Prepare an approximately 0.042 N sodium thiosulfate solution and stabilize with sodium furoate according to Platow (6). Add to each liter of solution a filtered solution of 1.0 g of furoic acid and 0.6 g of sodium carbonate.

Standardize the sodium thiosulfate solution against either potassium iodate or potassium bromate each time before using. To a 25 ml portion of standard iodate or bromate solution add 10 ml of 4 N sulfuric acid and sufficient potassium iodide for complete reduction of the oxidizing agent and for solution of the liberated iodine. When using the bromate standard, add 4 or 5 drops of the ammonium molybdate solution to catalyze the oxidation of iodide. Use starch as the indicator when titrating the liberated iodine with the sodium thiosulfate solution.

Sodium Cobaltinitrite. Use solid sodium cobaltinitrite, free of potassium.

Starch. Prepare a starch indicator solution according to Kolthoff and Sandell (3). To a liter of boiling water add a water suspension of 2 g of soluble starch plus 10 mg of mercuric iodide to serve as a preservative. Heat the solution until clear and then filter.

EXPERIMENTAL

The analytical weights were calibrated against Class M weights previously calibrated by the National Bureau of Standards. All weighings involved in the various standardizations were corrected for air buoyancy.

Calibrated Normax volumetric equipment was used in all cases. Standard solutions were calculated to 20° C; when these solutions were used at other temperatures, corrections were made for the changes in the volumes of these solutions.[2] Likewise the temperatures of the ocean water samples at the time of analysis were recorded so that the amount of potassium per kilogram of the sea water could be calculated.

To avoid introduction of errors in the calculated results due to lack of significant figures in the volumes of the sodium thiosulfate solution used, the normality of the titrant was adjusted so that the titration volumes usually fell between 40 and 50 ml. The titrant was always standardized against two independent standard solutions and check values differing by no more than 0.1% were demanded.

The silver nitrate solution, prepared to be about 0.28 N, was standardized against two reference standards. In one case, weighed amounts of recrystallized sodium chloride, dried at 390° C for 12 hours, were used as the standard. A correction factor of 1.00045, as pointed out by Sverdrup *et al.* (9, p. 52) was used for converting the chlorine equivalent to the chlorinity. The other standard was the Normal Sea Water prepared by the Hydrographical Laboratories in Denmark. Results by these two standardizations agreed to within less than 0.005 chlorinity unit. Checks to within less than 0.010 chlorinity unit were demanded in the chlorinity determinations on the sea water samples.

It was found that much of the calcium in the ocean water samples taken for analysis was precipitated as calcium sulfate in the 50% alcohol solution during the precipitation of the potassium-sodium cobaltinitrite. This had no undesirable effect on the subsequent iodimetric estimation of potassium.

The 1952 International Atomic Weights were used in all calculations (14).

DISCUSSION OF RESULTS

The results of the various analyses of sea water samples are presented in Table III. These samples had been obtained from a number

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[2] The correction factor was d_t/d_{20}, where d_{20} is the density of water at 20° C and d_t the density of water at the other temperature.

TABLE III. THE POTASSIUM-CHLORINITY RATIO OF OCEAN WATER

Labrador Sea, Atlantic Ocean; Lat. 60° 17' N, Long. 59° 41' W; April 28, 1950

Depth Meters	K °/oo	Cl °/oo	K/Cl
1	0.3800	18.878	0.02013
197	0.3894	19.262	0.02022
	0.3889		0.02019
984	0.3897	19.311	0.02018

Gulf Stream, Atlantic Ocean; Lat. 32° 30' N, Long. 77° 14.5' W; February 26, 1950

0	0.4039	20.034	0.02016
37	0.4039	20.018	0.02018
	0.4046		0.02021
	0.4036		0.02016
419	0.4036	19.974	0.02021

Sargasso Sea, Atlantic Ocean; Lat. 32° 18' N, Long. 64° 31' W; January 13, 1950

471	0.4050	20.082	0.02017

Off Lower California, Pacific Ocean; Lat. 24° 48.5' N, Long. 116° 40' W; February 3, 1950

0	0.3780	18.730	0.02018
200	0.3858	19.106	0.02019
1000	0.3857	19.113	0.02018

Lat. 28° 40.5' N, Long. 122° 46' W.

0	0.3779	18.711	0.02020
200	0.3759	18.639	0.02017
2000	0.3871	19.159	0.02020

Lat. 29° 36.5' N, Long. 116° 19.5' W.

0	0.3758	18.570	0.02024
200	0.3810	18.827	0.02024
	0.3791		0.02014
1200	0.3858	19.116	0.02018

Off Washington Coast, Pacific Ocean; Lat. 47° 25' N, Long. 126° 17' W; March 14, 1952

100	0.3731	18.521	0.02014
1000	0.3844	19.092	0.02013
	0.3851		0.02017
1800	0.3871	19.212	0.02015

Lat. 47° 50' N, Long. 127° 29' W; May 2, 1952

0	0.3659	18.103	0.02021
100	0.3711	18.412	0.02016
1000	0.3847	19.063	0.02018
2000	0.3869	19.143	0.02021

TABLE III (continued)

Off Vancouver Island, Pacific Ocean; Lat. 49° 10′ N, Long. 128° 48′ W; May 5, 1952

Depth Meters	K°/oo	Cl°/oo	K/Cl
1000	0.3802	18.854	0.02017
2000	0.3869	19.130	0.02022

Hein Bank, Strait of Juan de Fuca; Lat. 48° 21.2′ N, Long. 123° 05.7′ W; March 12, 1952

Depth Meters	K°/oo	Cl°/oo	K/Cl
0	0.3437	17.036	0.02017
10	0.3459	17.145	0.02018
50	0.3478	17.212	0.02021
	0.3468		0.02015
135	0.3563	17.666	0.02017

East Sound, Orcas Island, Washington; Lat. 48° 41′ N, Long. 122° 54′ W; July 10, 1951

Depth Meters	K°/oo	Cl°/oo	K/Cl
0	0.3278	16.220	0.02021
23	0.3429	16.974	0.02020

Lat. 48° 37′ N, Long. 122° 51′ W; July 10, 1951

Depth Meters	K°/oo	Cl°/oo	K/Cl
27	0.3458	17.085	0.02024

Off Point Jefferson, Puget Sound; Lat. 47° 45.5′ N, Long. 122° 24.8′ W; March 11, 1952

Depth Meters	K°/oo	Cl°/oo	K/Cl
0	0.3279	16.248	0.02018
20	0.3312	16.419	0.02017
50	0.3326	16.453	0.02022
100	0.3337	16.537	0.02018
200	0.3342	16.576	0.02016

Mean of all samples   0.02018, $S_1{}^a$ = 0.000,028
Correction   +0.00005, S_1 = 0.000,015
Corrected Ratio   0.02023, S_3 = 0.000,032[b]

[a] S = Standard deviation.
[b] See equation (1).

of widely separated stations in the Atlantic and Pacific Oceans as well as from the inland waters of the Puget Sound Region.

The precision and accuracy of the potassium determination have been evaluated elsewhere by the authors (2). For the amount of potassium (8–10 mg) taken for analysis in a 25 ml sample of sea water, the precision is approximately ± 0.1% and the accuracy is approximately −0.25 ± 0.075%. The negative value for the accuracy is significant. It denotes a small systematic solubility error for

which a correction may be applied to experimental results. The value ± 0.075 is the mean deviation of this error.

It has been shown by Jacobsen and Knudsen (1) that a precision and accuracy of about ± 0.05% may be attained with very careful work for the chlorinity determination. The data of the present study support this value; however, to be conservative, we have considered that the chlorinity data of the present work have a precision and accuracy of about ± 0.067%.

In Table III the potassium-chlorinity ratio has been calculated for each sample of sea water. The mean of all ratios and the standard deviation have been calculated to be 0.02018 ± 0.000,028, respectively, with no significant regional differences being evident. This mean ratio has been corrected for the solubility error mentioned above. The corrected potassium-chlorinity ratio of sea water then becomes 0.02023 ± 0.000,032. The new value of the standard deviation, s_x, was calculated from the expression

$$s_x = \sqrt{s_a{}^2 + s_b{}^2} \qquad (1)$$

where s_x = standard deviation of the sum x; s_a = standard deviation of a; s_b = standard deviation of b, as given by Vignau (12) for the standard deviation of the sum $x = a + b$. The precision (standard deviation) of the corrected ratio, 0.000,032 or 1.6 parts per 1,000, compares favorably with the precisions for the ratios given in Table I; only the ratio of magnesium/chlorinity has as favorable a precision.

It is possible to calculate what the standard deviation of the potassium-chlorinity ratios should be from the established standard deviations for the determinations of potassium and chlorinity. Using the values given previously, the expected standard deviation has been calculated to be 0.000,024 from the expression given by Vignau (12) for the standard deviation of the quotient $x = a/b$:

$$s_x = \frac{\sqrt{(b \times s_a)^2 + (a \times s_b)^2}}{b^2} \ .$$

This calculated value compares well with the experimental value of the standard deviation, 0.000,028, and indicates that the application of this method to sea water is valid. The precision of these results is as good as or better than that for the ion-chlorinity ratios determined for the other major ions in sea water.

The corrected value of 0.02023 for the potassium-chlorinity determination established in the present investigation agrees closely with the value 0.02029 based on Dittmar's work and corrected by Lyman

and Fleming (4) and Webb (13), but it differs considerably from the values obtained by other investigators listed in Table II.

ACKNOWLEDGEMENT

LITERATURE CITED

1. JACOBSEN, J. P. AND M. KNUDSEN
    1940. Urnormal 1937 or primary standard sea water 1937. Publ. sci. Ass. Océanogr. phy., No. 7, Liverpool. 38 pp.
2. JENTOFT, R. E. AND R. J. ROBINSON
    1956. The determination of potassium as the metaperiodate. Anal. Chem., *28:* 2011–2015.
3. KOLTHOFF, I. M. AND E. B. SANDELL
    1952. Textbook of Quantitative Inorganic Analysis. 3rd ed. Macmillan Co., New York. 759 pp.
4. LYMAN, JOHN AND R. H. FLEMING
    1940. Composition of sea water. J. mar. Res., *3:* 134–146.
5. MIYAKE, Y.
    1939. Chemical studies of the western Pacific Ocean. I and II. Bull. chem. Soc. Japan, *14:* 29–35, 55–58.
6. PLATOW, A. M.
    1939. Sodium furoate as a preservative for analytical solutions. Chem. Anal., *28:* 30.
7. ROBINSON, R. J. AND F. W. KNAPMAN
    1941. The sodium-chlorinity ratio of ocean waters from the northeast Pacific. J. mar. Res., *4:* 142–152.
8. SCOTT, W. W.
    1939. Standard methods of chemical analysis. 5th ed. Van Nostrand and Co., New York. 2617 pp.
9. SVERDRUP, H. U., M. W. JOHNSON and R. H. FLEMING
    1942. The oceans. Prentice-Hall Inc., New York. 1087 pp.
10. THOMPSON, T. G., W. R. JOHNSON AND H. W. WIRTH
    1931. The sulfate-chlorinity ratio in ocean waters. J. Cons. int. Explor. Mer, *6:* 246–251.
11. THOMPSON, T. G. AND C. C. WRIGHT
    1930. Ionic ratios of the waters of the north Pacific Ocean. J. Amer. chem. Soc., *52:* 915–921.

12. Vignau, M.
 1950. Statistical methods applied to analytical chemistry. Chim. Anal., *32:* 35–41.
13. Webb, D. A.
 1939. The sodium and potassium content of sea water. J. exp. Biol., *16:* 178–183.
14. Wichers, E.
 1952. Report of the Committee on Atomic Weights of the American Chemical Society. J. Amer. chem. Soc., *74:* 2447–2450.
15. Willard H. H. and A. J. Boyle
 1941. Determination and separation of potassium as periodate. Industr. Engng. Chem., Anal. Ed., *13:* 137–139.