THE SODIUM-CHLORINITY RATIO OF OCEAN WATERS FROM THE NORTHEAST PACIFIC

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Ocean water is a complex solution of many ions. The concentration of this solution varies considerably from place to place but it has been repeatedly shown that the relative concentration of the ions to each other is remarkably constant. The composition of an average water sample having a chlorinity of 19.374 °/₀₀ is given by Thompson (*5*) as follows:

TABLE I

COMPOSITION OF AN OCEAN WATER, Cl = 19.374 °/₀₀

Cations	*Grams per Kilogram*	*Equivalents per Liter*
Na^+	10.722	0.4662
Mg^{++}	1.297	0.1067
Ca^{++}	0.417	0.0209
K^+	0.382	0.0098
	12.818	0.6036
Anions	*Grams per Kilogram*	*Equivalents per Liter*
Cl'	19.337	0.5453
SO_4''	2.705	0.0564
HCO_3'	0.097	0.0016
CO_3''	0.007	0.0002
Br'	0.066	0.0008
	22.212	0.6043

Sodium is by far the outstanding major cation and it would be supposed that its relative concentration, expressed as the sodium-chlorinity ratio, would be quite accurately known. There has been, however, considerable difference of opinion in regard to this ratio as the following summary (*6*) shows:

TABLE II

SUMMARY OF PREVIOUS WORK

Investigator	*Location*	*Number of Samples*	*Na/Cl Ratio (by Weight)*
Dittmar	All, except Polar	77	0.5514
Makin	Atlantic	22	0.5476
Schloesing	Atlantic and Mediterranean	3	0.5528
Thorpe and Morton	Irish	1	0.5573
Schmidt	Baltic and White	6	0.5536
Steiger	Atlantic	1	0.5567
Wheeler	Atlantic	5	0.5567
Schmelck	Atlantic	51	0.5504
Forsberg	Siberian	4	0.5484
Natterer	Mediterranean	42	0.5310
Kolotoff	Black Sea	1	0.5518
Anderson and Thompson	Puget Sound	12	0.5495
		225	
		Weighted Average	0.5509
		Mean	0.5523

The reasons for these variations may be partly due to the manner of storing the samples and the methods of analyses. In general, sodium in sea water has been determined by indirect methods. The total sulfate method, as first used by Dittmar (*2*) and followed by many others listed in Table II, consisted of taking a known weight of sea water and evaporating it to dryness with dilute H_2SO_4 to obtain the weight of the normal sulfates. Separate determinations of Ca, Mg, and K upon the same sample made it possible to calculate the weight of the Na_2SO_4 found. The chief criticism lies in the dependence of the Na determination upon the accuracy of the other determinations.

More recently Webb (*7*) proposed the Na/Cl ratio of 0.5549($\pm$0.001) as the result of analyses performed on a sample of Firth of Clyde sea water having a Cl of 18.43 $^{\circ}/_{\circ\circ}$. He used a modification of the zinc uranyl acetate method as given by Robertson and Webb (*4*). As further evidence in support of this ratio, Webb computed a Na/Cl ratio of 0.5554 ($\pm$0.001) by using the SO_4/Cl, Ca/Cl, Mg/Cl, and K/Cl ratios and the excess base data generally accepted. Also, from the relationship between chlorinity and salinity, he computed a Na/Cl ratio of 0.5580 which, although probably too high due to difficulty in making accurate determinations of salinity, he believes provides confirmatory evidence supporting the higher of the several ratios hitherto suggested by the work of previous authors.

Lyman and Fleming (*3*) critically examined the results of determinations of the major ions of sea water and suggested "best values" for the various ratios with chlorinity. Knowing the values of the other main constituents they calculated sodium by difference. This value resulted in a Na/Cl ratio of 0.5556.

PREPARATION OF REAGENTS AND STANDARD SOLUTIONS

For the present study, the method of analysis was the zinc uranyl acetate procedure first introduced by Barber and Kolthoff (*1*), and applied to ocean waters by Robertson and Webb (*4*).

Zinc Uranyl Acetate:

(A) Dissolve 80 grams of $UO_2\ (C_2H_3O_2)_2 \cdot 2H_2O$ with heating in 425 ml. of water to which has been added 14 ml. of glacial $HC_2H_3O_2$.

(B) Dissolve 220 grams of $Zn\ (C_2H_3O_2)_2 \cdot 2H_2O$ with heating in 275 ml. of water to which has been added 7 ml. of glacial $HC_2H_3O_2$.

Mix solutions (A) and (B) while hot and set aside for 24 hours. Filter the solution into a Pyrex bottle and add a small amount of $NaC_2H_3O_2$ to saturate the reagent with $NaZn(UO_2)_3(C_2H_3O_2)_9$. Set the reagent aside for at least 24 hours and filter each quantity just before using.

Ethyl Alcohol:

Saturate 95% C_2H_5OH with $NaZn(UO_2)_3(C_2H_3O_2)_9$ and filter just before using.

NaCl Solutions:

The NaCl was precipitated from a saturated solution of the C. P. salt with HCl gas. It was further purified by recrystallization from water, and after drying was ignited in a platinum dish at a temperature of 500 to 600° C.

Sufficient pure, dry NaCl was dissolved in water to make a solution containing 10.70 mg. of Na per ml.

Synthetic Sea Water Solutions:

Pure $MgSO_4$, $MgCl_2$, $CaCl_2$, and KCl were dissolved in water and diluted to 500 ml. Analysis of a 25 ml. portion of this solution indicated either a negligible or a very small amount of sodium present. Pure NaCl was added to the remainder of the solution and it was diluted to 1 liter. Sufficient amounts of the salts were taken so that the concentration of the ions in the final solution was equivalent to that in a water of Cl = 19.374 ‰.

PROCEDURES

Determination of Sodium:

Thoroughly wash a sintered glass crucible of porosity 20 to 30 μ with distilled water, followed by a few ml. of acetone, and finally by anhydrous ether. Remove all trace of ether from the crucible by passing air through it for about two minutes. Place the uncovered crucible in the balance case and weigh after 15 minutes.

Weigh 1 ml. of a filtered water sample in a covered 25 ml. beaker. To the weighed sample add the previously filtered zinc uranyl acetate reagent. Stir thoroughly for two minutes and then set the beaker aside for one and one-half hours. The exact volume of reagent to be used should be 10 or more times greater than the volume of the sample. In the present work, 13 ml. were used per sample.

Filter the precipitate into the crucible. Because of the high solubility coefficients of $NaZn(UO_2)_3(C_2H_3O_2)_9$, the temperature of filtering the reagents and the precipitate should be approximately the same. Use 10 ml. of the filtered C_2H_5OH reagent to wash and transfer the precipitate to the crucible. Dry the precipitate with 10 ml. of anhydrous ether added in several portions. Remove all trace of ether and weigh as before.

The composition of the precipitate is $NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$. Multiply the weight of the precipitate by the factor 0.01495 to obtain the weight of the Na in the sample. Convert this value to Na °/₀₀. The weighings were not corrected to in vacuo since this involved a correction of only 6 parts per 10,000 which would have an insignificant effect.

Determination of Chlorinity:

The well known Mohr volumetric procedure as adapted to sea water was used in the determination of the chlorinity. The chlorinity of check determinations was required to agree within 0.012 °/₀₀. The silver nitrate solution was standardized with Normal Water prepared by the Hydrographic Laboratories of Copenhagen.

COLLECTION AND ANALYSES OF SAMPLES

A total of 99 samples were collected for analyses by the M. S. CATALYST of the Oceanographic Laboratories of the University of Washington. Vertical series of samples were taken from three Pacific Ocean stations off the coast of Washington, two stations in the Strait of Juan de Fuca, and five stations from various portions of Puget Sound.

The samples were stored in paraffin-lined bottles and were analyzed usually within a few days of the time of collection. With each group of six sea water samples analyzed, one sample of a standard synthetic sea water solution was included. Thus the method was under careful control at all times.

RESULTS OF ANALYSES

Known Solutions:

Thirty-seven analyses of synthetic sea water solutions were made. The mean error of these determinations was -0.1%, and the average deviation from this mean was $\pm 0.2\%$. In Table III a representative sampling of these results is given. In Table III also are given the results of 5 analyses of NaCl solutions. The mean error of these determinations is essentially the same as that found for the synthetic sea water. Using this same method with NaCl solutions, Barber and Kolthoff (*1*) found errors ranging from -0.2% to $+0.7\%$. They concluded that the method gave results accurate to about 0.5%. Robertson and Webb (*4*) in analyzing NaCl solutions and synthetic sea water by this method reported errors ranging from -0.5% to $+0.4\%$, with a probable error of 0.2%.

The results of the analyses of the 45 samples from the three Pacific Ocean stations are given in Table IV. The Na content was found to range from 9.73 to 10.67 grams per kilogram of water. The mean Na/Cl ratio was calculated to be 0.5549. In Table V are given the results of the analyses of the 53 samples from the seven stations located in the Strait of Juan de Fuca and in Puget Sound. The sodium content ranged from 8.98 to 10.42 grams per kilogram of water, with the exception of one sample (Brown Point, surface, for which the Na $^{\circ}/_{\circ\circ}$ was 7.24). The mean Na/Cl ratio for these samples was found to be 0.5562.

For the 98 samples analyzed in all, the mean Na/Cl ratio was 0.5556. These main ratios are thought to have an accuracy of about 0.0005 with a mean deviation of 0.001.

EVALUATION OF RESULTS

The method yielded satisfactory results with synthetic sea water for the range of concentrations comparable to the Na concentration of the samples analyzed. However, observation of the results shows slightly high results for the more dilute samples of synthetic sea water and slightly low results for the more concentrated solutions. In general, this trend is summarized as follows:

Na °/₀₀	Cl °/₀₀	% Error
9.0– 9.4	16.0–16.7	+0.2
9.4– 9.7	16.7–17.2	+0.1
9.7–10.4	17.2–18.4	0.0
10.4–10.7	18.4–19.0	−0.1

A trend is quite evident but the errors are somewhat variable and relatively small. Consequently no corrections have been incorporated in the listed results for Na in sea water.

The calculated Na/Cl ratios for the more dilute waters of Puget Sound are slightly larger than for the Pacific Ocean. However, if these values are corrected in accordance with the errors just discussed the mean Na/Cl ratios for the Pacific Ocean samples become 0.5553 and for the Strait of Juan de Fuca and Puget Sound become 0.5555. It should be pointed out, though, that the actual results differ from these corrected results within the limits of experimental error for the method.

The value of the Na/Cl ratio for the Pacific Ocean samples, 0.5549 is identical with Webb's (*7*) value for the Firth of Clyde sample. The mean Na/Cl ratio of 0.5556 for all samples in this study is identical with the "best value" suggested by Lyman and Fleming (*3*), and is almost identical with the Na/Cl ratio of 0.5554 computed by Webb from the accepted data of the major ions present in sea water. When compared with analyses made by the total sulfate method, the Na/Cl ratio found in this study is higher than the mean ratio of 0.5523 given in Table II. However, some of the higher values given in that table do not differ greatly from 0.5556. The direct determination of sodium is thought to be more accurate than calculation by indirect methods.

SUMMARY

The sodium content of synthetic sea water and NaCl solutions was determined by means of the zinc uranyl acetate method. The mean error found for these known solutions was −0.1% with an average deviation from this mean of ± 0.2%.

The sodium content of sea water samples was determined and the following values for the Na/Cl ratio were calculated:

(A) for 46 samples from three Pacific Ocean stations off the coast of Washington,—0.5549.

(B) for 53 samples from seven stations located in the Strait of Juan de Fuca and Puget Sound,—0.5562.

(C) for the total 99 samples from the ten stations from the Pacific Ocean, Strait of Juan de Fuca, and Puget Sound,—0.5556.

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TABLE III

Determination of Sodium in Solutions of Known Concentration

NaCl Solutions

Mg. Na Taken	*Mg. Na Found*	*% Error*
10.51	10.49	−0.2
10.41	10.39	−0.2
10.33	10.30	−0.3
10.16	10.14	−0.2
9.89	9.86	−0.3

Synthetic Sea Water

Mg. Na Taken	*Mg. Na Found*	*% Error*
10.72	10.70	−0.2
10.68	10.67	−0.1
10.65	10.62	−0.3
10.29	10.29	0.0
9.99	9.97	−0.2
9.72	9.73	+0.1
9.56	9.57	+0.1
9.31	9.34	+0.3
7.81	7.86	+0.6

TABLE IV

THE SODIUM-CHLORINITY RATIO IN PACIFIC OCEAN WATERS OFF THE COAST OF WASHINGTON

Lat. 47° 40′ N. Long. 126° 20′ W.

July 24, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.73	17.50	0.556
10	9.76	17.60	0.555
20	9.76	17.60	0.555
30	9.80	17.66	0.555
50	9.94	17.91	0.555
75	10.00	17.99	0.556
100	10.19	18.34	0.556
200	10.41	18.76	0.555
300	10.42	18.78	0.555
400	10.43	18.82	0.554
500	10.45	18.89	0.553
800	10.52	18.98	0.554
1000	10.59	19.04	0.556
1200	10.60	19.10	0.555
1500	10.60	19.12	0.555

Lat. 47° 09′ N. Long. 126° 20′ W.

July 25, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.82	17.71	0.555
10	9.84	17.73	0.555
20	9.83	17.73	0.554
30	9.91	17.85	0.555
50	9.98	17.96	0.555
75	9.96	17.97	0.554
100	9.97	18.01	0.554
200	10.39	18.78	0.553
300	10.39	18.78	0.553
400	10.44	18.84	0.554
500	10.45	18.89	0.553
800	10.51	18.99	0.554
1000	10.55	19.05	0.554
1500	10.60	19.11	0.555
2000	10.64	19.17	0.555

TABLE IV (*Cont.*)

Lat. 47° 09′ N. Long. 126° 49′ W.

July 25, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.88	17.79	0.555
10	9.88	17.79	0.555
20	9.92	17.89	0.555
30	—	—	—
50	9.98	17.98	0.555
75	9.98	17.98	0.555
100	10.01	18.03	0.555
200	10.39	18.75	0.554
300	10.46	18.82	0.556
400	10.44	18.84	0.554
500	10.51	18.90	0.556
800	10.55	19.00	0.555
1000	10.60	19.05	0.556
1200	10.60	19.07	0.556
1500	10.62	19.12	0.555
2000	10.67	19.17	0.556

TABLE V

THE SODIUM-CHLORINITY RATIO IN WATERS OF THE STRAIT OF JUAN DE FUCA AND PUGET SOUND

Neah Bay, Strait of Juan de Fuca

Lat. 48° 25′ N. Long. 124° 27′ W.

July 6, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.29	16.69	0.557
10	9.62	17.28	0.557
20	9.96	17.90	0.556
30	10.28	18.46	0.557
50	10.31	18.57	0.555
100	10.37	18.67	0.555
150	10.42	18.78	0.555
250	10.42	18.80	0.554

TABLE V (*Cont.*)

Pillar Point, Strait of Juan de Fuca

Lat. 48° 18′ N. Long. 124° 03′ W.

November 2, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.66	17.37	0.556
10	9.67	17.39	0.556
20	9.69	17.43	0.556
30	9.75	17.56	0.555
50	9.79	17.63	0.555
75	9.90	17.82	0.555
100	9.92	17.86	0.555
150	10.27	18.49	0.555
175	10.26	18.53	0.554

Point No Point, Puget Sound

Lat. 47° 54′ N. Long. 122° 29′ W.

November 1, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.43	16.93	0.557
10	9.43	16.93	0.557
20	9.41	16.94	0.556
30	9.42	16.94	0.556
50	9.44	16.96	0.557
75	9.43	16.96	0.556
100	9.44	16.96	0.556
184	9.43	16.98	0.555

Jefferson Head, Puget Sound

Lat. 47° 45′ N. Long. 122° 28′ W.

November 1, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.20	16.53	0.557
10	9.36	16.84	0.556
20	9.39	16.87	0.556
30	9.39	16.91	0.555
50	9.40	16.91	0.556
75	9.42	16.94	0.556
100	9.42	16.95	0.556
200	9.46	17.01	0.556
247	9.46	17.00	0.556

TABLE V (*Cont.*)

Brown Point, Puget Sound

Lat. 47° 19′ N. Long. 122° 28′ W.

July 10, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	7.24	12.99	0.557
10	9.04	16.23	0.557
20	9.05	16.26	0.557
30	9.07	16.27	0.557
50	9.06	16.28	0.556
100	9.17	16.48	0.556
170	9.22	16.58	0.556

Fosdick Point, Puget Sound

Lat. 47° 15′ N. Long. 122° 35′ W.

July 10, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	9.00	16.15	0.557
10	9.01	16.17	0.557
20	9.02	16.19	0.557
30	9.02	16.17	0.557
50	9.03	16.22	0.557
74	9.04	16.27	0.556

Devils Head, Puget Sound

Lat. 47° 10′ N. Long. 122° 46′ W.

July 9, 1940

Depth meters	*Na* °/oo	*Cl* °/oo	*Na/Cl*
S	8.99	16.12	0.558
10	8.98	16.11	0.557
20	8.99	16.14	0.557
30	8.99	16.14	0.557
50	9.01	16.15	0.558
93	9.01	16.19	0.557