Chemical Studies of the Western Pacific Ocean. I. The Chemical Composition of the Oceanic Salt. Part 1.

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Under the guidance of Prof. Okada, Director of the Central Meteorological Observatory of Japan, a thorough investigation of the Western Pacific Ocean is now being contemplated. The present author, being charged with the chemical survey in this project, intends to determine first the chemical composition of the sea salt, precision in analyses being esteemed above all. The present paper records the results of the chemical analyses of the sea salt.

Today, we have a large number of reliable determinations(1) of the chemical composition of oceanic salt, among which W. Dittmar's seventy-seven analyses of samples of water collected from various localities and depths in the memorial "Challenger"-Expedition, are still highly regarded for their exactness. We can easily see in these numerous analyses that there is an astonishing close agreement among them. However, contemporary geochemistry is not satisfied with such mere agreement, and requires the delicate differences between them to the accuracy of the second order. In such minute differences, we have a possibility of perceiving the true sources and cycles of the elements occurring in the sea which are quite obscure even at the present time. In spite of numerous active chemical investigations in oceanography, these being mainly in the domains of fishery and chemical industry, accurate chemical analysis of waters from the Pacific Ocean near Japan has not yet been made from the stand point of exact analytical chemistry.

Samples of Sea Water. The dates and positions of collection are shown in Table 1.

Table 1.

No.	Date	Position		No.	Date	Position	
		Lat. N	Long. E			Lat. N	Long. E
31	Oct. 10, 1937.	24°53′	125°53′	61	Dec. 1, 1937	27°23′	136°48′
32	,, 10, ,,	25°25′	126°48′	62	,, 2, ,,	25°46′	137°17′
36	,, 11, ,,	27°25′	129°45′	64	,, ,, ,,	24°42′	137°50′
38	,, 12, ,,	29°12′	131°53′	67	,, ,, ,,	24°36′	139°27′
40	,, ,, ,,	30°28′	133°32′	70	,, 4, ,,	25°02′	141°30′
42	,, ,, ,,	31°13′	134°29′	73	,, 8, ,,	27°32′	141°58′
45	,, 13, ,,	33°05′	137°01′	75	,, 9, ,,	29°38′	140°56′
56	Nov. 30, ,,	32°40′	137°50′	76	,, ,, ,,	30°09′	140°40′
57	Dec. 1, ,,	30°04′	136°40′	81	,, 10, ,,	33°08′	139°49′

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(1) F.W. Clarke, "The Data of Geochemistry," 126, Washington (1924).

Methods of Analysis. The analytical procedures adopted will be briefly described in the following paragraphs.

(1) *Chlorinity*. The chloride determination of sea water is one of the most important problems in oceanographical research. The analytical method which is now internationally accepted, is M. Knudsen's system, in which Mohr's argentometry is adopted as a chemical procedure. We can determine the chloride content of sea water very easily, by Knudsen's volumetrical apparatus, the normal sea water supplied from his laboratory, and his hydrographical tables. However, this system has a very serious weakness in its analytical procedure. Mohr's argentometry needs much improvement from the stand point of today's analytical chemistry.(2)

There are two large sources of errors in this method of titration, one is due to the strong colloidal nature of the silver chloride precipitate, and the sign of this error tends to be minus while the other is a plus one which comes from the sensibility of the indicator. The latter is always about 0.15%, if the titration is done under a careful control, although it has no effect on the determination of chloride of sea water. On the other hand, the former is always larger and more serious, because its magnitude varies with the analytical conditions, i.e. the concentration of the solution, the rate of stirring, the velocity of the titration, etc. To obtain good results, one must stir the solution just enough during the titration, and one must not cease stirring before ascertaining that the red colour indicating the end point will not disappear again.

Fluorescein or its sodium salt uranin, for which we are indebted to K. Fajans and his collaborator, is a superior adsorption indicator for the chloride determination. Kolthoff(3) and Böttiger(4) stated that the argentometric titration with this indicator is very accurate when compared with the potentiometric titration. The present author has also verified the superiority of this indicator. He has contrived to use this dyestuff for the chloride determination of sea water, and obtained very satisfactory results. The indicator used is a mixture of 5 c.c. of 0.1% uranin solution and 100 c.c. of 1% starch solution, the starch serving as a protective colloid; and 2 c.c. of this indicator is added to each 15 c.c. of sea water.

Although the new indicator is used instead of potassium chromate, it is not at all necessary to change any other procedure of Knudsen's system. At any rate it is important that this improvement makes the best use of his hydrographical tables and his volumetric apparatus. The mean error of the titration with this new indicator is always under 0.015%, and the time needed for each titration is shorter than one half of that required for Mohr's method. Since the colour change at the end point is quite clear, and owing to the protective colloid, there is no danger of under titration caused by the too early appearance of the end point.

Burettes and pipettes, made according to Knudsen's type by Fujiwara Brothers and Co., were accurately calibrated.

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(2) Lottermoser and Lorenz, *Kolloid-Z.*, **68** (1934), 201.

(3) I.M. Kolthoff and L.H. van Berk, *Z. anal. Chem.*, **70** (1927), 369.

(4) W. Böttiger and K.O. Schmidt, *Z. anorg. allgem. Chem.*, **137** (1924), 246.

(2) *Sodium and potassium.* A 30 c.c. sample of sea water was taken with a pipette; the sulphate ion was removed in the present of acid with a solution of barium chloride; and the excess of barium chloride with calcium and magnesium was completely precipitated as carbonates and filtered off. After weighing the total chlorides of alkalies as usual, potassium was determined in the form of potassium chloroplatinate.

(3) *Calcium and magnesium.* A 100 c.c. portion of sea water was taken. First, after adding ammonium chloride containing a little ammonia, calcium oxalate was precipitated by boiling with ammonium oxalate. The precipitation was repeated two or three times in order to remove the occluded magnesium as much as possible. Calcium oxalate was filtered off; the precipitation was repeated. Finally it was ignited to calcium oxide. Weighing was done with due care of its hygroscopic nature.

Magnesium was determined with the filtrate from the calcium determination by the magnesium ammonium phosphate method: the precipitation was repeated and then ignited to magnesium pyrophosphate.

(4) *Sulphate.* A 30 c.c. sample was taken; a little hydrochloric acid was added; and the sulphate ion was precipitated by boiling with barium chloride. The precipitate of barium sulphate was allowed to settle down by standing for several hours and was then filtered through the finest filter (Swedish filtering paper No. 00). It was thoroughly washed with hot water until no chloride ion was detectable in the filtrate and then ignited to a constant weight.

(5) *Carbonate.* Although we could obtain undoubtedly a more accurate result by the back titration method for the determination of total carbonate ion in sea water than by direct titration, the latter method was used. A 100 c.c. portion of sea water was titrated with a standard hydrochloric acid solution with methyl orange as the indicator.

(6) *Bromine.* The determinations of this element with several gravimetric methods were tried many times without success owing to the small amount of free chlorine usually produced together with bromine, the values being apt to be too high. The colorimetric method (the method of W. J. Dibdin and L. H. Cooper⁽⁵⁾) was finally successful, which, however, is not so accurate as the gravimetric method.

(7) *Strontium and boron.* Strontium and boron in sea water were also determined. The details of the results will be published in the following paper.

The Results of the Analyses. Table 2 shows the results of the analyses, in which each element is expressed in number of grams per kilogram of sea water. Strontium is included in the weight of calcium. Likewise, only the chlorinity is mentioned here instead of chlorine and bromine.

The Composition of the Sea Salt from the Western Pacific. The percentage composition of oceanic salt, which has been computed from the data of total analysis mentioned above, is shown in Table 3. We can see

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(5) F.D. Snell and C.T. Snell. "Colorimetric Methods of Analysis," 544, New York (1936).

that a very similar result has been obtained in each analysis, regardless of the position of securing the sample. This agreement seems to indicate a homogeneity in the composition of the sea salt of the Western Pacific Ocean.

Table 2.

No.	Chlorinity	SO_4	CO_3	Ca	Mg	Na	K
31	19.29	2 6973	0.0710	0.4276	1.3023	10.5795	0.3787
32	19.27	2.6893	0.0698	0.4295	1.2967	10.6457	0.3693
36	19.22	2 6734	0.0710	0.4253	1.2978	10.5937	0.3663
38	19.17	2.6790	0.0701	0.4234	1.2989	10.5018	0.3875
40	19.13	2.6657	0.0681	0.4225	1.2931	10.5308	0.3682
42	19.10	2.6658	0.0698	0.4263	1.2989	10.4320	0.3706
45	18.91	2.6531	0.0701	0.4218	1.2853	10.4038	0.3232
56	19.15	2.6925	0.0698	0.4264	1.2993	10.4439	0.3752
57	19.23	—	0.0701	0.4249	1.2971	—	—
61	19 19	—	0.0700	0.4266	1.2935	10.6183	0.3605
62	19.17	2.6820	—	—	—	—	—
64	19 15	2.6710	0.0671	0.4271	1.2908	10.6118	0.3272
67	19.22	2.6708	—	—	—	—	—
70	19.22	2.6975	0.0701	0.4235	1.2958	10.5477	0.3826
73	19.28	—	0.0701	0.4228	1.3052	10.5715	0.3760
75	19.18	2.6656	—	—	—	—	—
76	19.13	—	0.0710	0.4272	1.2962	10.5109	0.3731
81	19.23	2.6902	0.0701	0.4269	1.3038	10.5809	0.3682
Average	19.17_7	2.6780_5	0.0698_8	0.4254_5	1.2969_8	10.5521_7	0.3661_6

Table 3.

No.	Cl	Br	CO_3	SO_4	Ca	Mg	Na	K
31	55.38	0.19	0.20	7.76	1.23	3.74	30.42	1.09
32	55.28	0.19	0.20	7.73	1.23	3.73	30.59	1.06
36	55.33	0.19	0.20	7.71	1.23	3.74	30.54	1.06
38	55.38	0.19	0.20	7.75	1.23	3.76	30.38	1.12
40	55.36	0.19	0.20	7.72	1.22	3.75	30.50	1.07
42	55.44	0.19	0.20	7.75	1.24	3.78	30.33	1.08
45	55.37	0.19	0.20	7.78	1.24	3.77	30.51	0.95
56	55.44	0.19	0.20	7.81	1.24	3.77	30.28	1.09
64	55.29	0.19	0.20	7.73	1.23	3.73	30.69	0.95
70	55.35	0.19	0.20	7.78	1.22	3.74	30.42	1.10
81	55.33	0.19	0.20	7.75	1.23	3.76	30.49	1.06
Average	55.35_9 $\pm 0.03_3$	0.19	0.20	7.75_2 $\pm 0.02_2$	1.23_1 $\pm 0.00_5$	3.75_2 $\pm 0.01_5$	30.46_8 $\pm$ 0.09_3	1.05_7 $\pm 0.03_7$

The Comparison of Compositions between the World's Average and the Western Pacific Ocean. From these results, we can obtain the average composition of the salt of the Western Pacific, taking into consideration the content of bromine, strontium and boric acid. In Table 4, the total salt composition of the Western Pacific is compared with those of the world's mean. For the average composition of the world, the values calculated by T. G. Thompson⁽⁶⁾ and by H. Wattenberg⁽⁷⁾ have been adopted, and also the analyses of W. Dittmar⁽⁸⁾ have been used as a reference. As seen from this table, the differences in the compositions between the world's average and the Western Pacific are very small, except that the values of sodium and potassium are a little lower, while on the contrary those of chloride and magnesium are but slightly higher, than the world's average. This tendency will become much clearer, when the amount of each component is represented as the number of mols per kilogram of water, assuming that the chlorinities are the same. In Table 5 the number of each element has been calculated when the chlorinity is $Cl = 19.374‰$

Table 4. The Percentage Compositions of the Oceanic Salt.

	Thompson	Wattenberg	Dittmar	Average	The Western Pacific
Na	30.60	30.43	30.59	30.52	30.47
Mg	3.70	3.72	3.73	3.73	3.74
Ca	1.19	1.19	1.20	1.19	1.19
Sr	0.04	0.04	—	0.04	0.04
K	1.09	1.11	1.11	1.10	1.06
Cl	55.18	55.14	55.29	55.17	55.31
SO_4	7.72	7.70	7.69	7.70	7.73
CO_3	0.30	0.40	0.21	0.30	0.20
Br	0.19	0.19	0.19	0.19	0.19
$B(OH)_3$	—	0.08	—	0.08	0.08

Table 5. The Number of Mols per kilo-gram Water. $Cl = 19.374‰$.

	Thompson	Wattenberg	Dittmar	Average	The Western Pacific
Na	0.4662	0.4638	0.4652	0.4651	0.4634
K	0.0098	0.0099	0.0093	0.0097	0.0095
Mg	0.0533	0.0535	0.0534	0.0534	0.0539
Ca	0.0104	0.0104	0.0105	0.0104	0.0104
Sr	—	0.00015	—	0.00015	0.00017
Cl	0.5454	0.5454	0.5454	0.5454	0.5454
Br	0.0008	0.00083	0.00083	0.0008	0.0008
SO_4	0.0281	0.0281	0.0280	0.0281	0.0282
CO_3	0.0017	0.0023	0.0012	0.0017	0.0012
$B(OH)_3$	0.00045	0.00045	—	0.00045	0.00043

In according with the custom of oceanography, the ratio of the number of the promilles of each element to the chlorinity has been calculated and compared in a like manner with the world's average (Table 6). Since the ratio of the chlorinity to the salinity is almost constant, the result of the comparison is naturally the same as that of Table 5.

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(6) T.G. Thompson, "Bulletin of the National Research Council, No. 85, Physics of the Earth. V. Oceanography," 69, New York (1932).

(7) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

(8) H.W. Harvey, "The Chemistry and Physics of Sea Water," 36, Camgridge (1928).

Table 6.

	Thompson	Wattenberg	Dittmar	Average	The Western Pacific
Na	0.55342	0.55105	0.55326	0.55258	0.54974 ± 0.001975
K	0.01971	0.02000	0.02007	0.01993	0.01909 ± 0.000620
Mg	0.06697	0.06746	0.06728	0.06719	0.06736 ± 0.000192
Ca	0.02152	0.02157	0.02170	0.02159	0.02155 ± 0.000067
SO_4	0.13962	0.13947	0.13908	0.13939	0.13967 ± 0.000375

A Comparison between the Western Pacific and the Northeastern Pacific. It is interesting to compare the salt compositions of the western and the northeastern parts of the Pacific Ocean. T. G. Thompson and his collaborators(9) have determined very precisely the salt compositions of the opposite side of the Pacific Ocean. The comparison of the chlorinity ratios on both sides of the ocean is shown in Table 7. It is quite noteworthy that there is an astonishing agreement between the analytical results of the west and the northeast. This agreement is by no means accidental, because the mean deviation of the analytical results are very small as shown in Table 3.

In spite of this good unity, however, we have to acknowledge the small, but significant discrepancy in the ratios of magnesium to the chlorinity. It will be investigated in the near future whether this discrepancy is substantial or not.

Table 7. A Comparison of Chlorinity Ratios of Elements in the Northeastern and the Western Pacific Ocean.

	Northeast	West
Na	0.5495	0.5497
K	0.0191	0.0191
Mg	0.0669	0.0676
Ca	0.02150	0.02155
SO_4	0.1396	0.1397

Summary.

(1) The major constituents of sea water from the Western Pacific Ocean near Japan have been quantitatively determined. The analytical results are as follows: the difference in the compositions between the world's average and the Western Pacific is very small, except that the values of sodium and potassium are a little lower, while those of chloride and magnesium are but slightly higher, in the latter than in the former.

(2) It is quite noteworthy that there is an astonishing agreement between the analytical results of the west and the northeast side of the Pacific Ocean.

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(9) *Loc. cit.*, p. 94-203.

(3) A new indicator has been used for the determination of chlorinity; that is a mixed solution of fluorescein and starch. The superiority of this indicator has been briefly discussed.

In conclusion, the author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

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