Chemical Studies of the Western Pacific Ocean. II.
The Chemical Composition of the Oceanic Salt. Part 2.*

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Methods of Analysis (*Continued*). *Strontium.* It is but lately that strontium was found to be the fifth in abundance among the metallic elements in sea water. Desgrez and Meunier(1) determined strontium in the waters of the English Channel by the spectroscopic method, in which the intensity of strontium line 4607 Å was compared with the reference line 4427 Å of iron. They obtained the result that the channel water contains 13.5 mg. of strontium per litre. T. G. Thompson and B. D. Thomas,(2) who recently repeated the spectroscopic analysis, ascertained the value of Desgrez and Meunier for this element.

It is interesting that the ratio of strontium to calcium in sea water is 0.033, which is considerably higher than the ratio 0.0059, calculated from the Clarke number. As has been discussed by H. Wattenberg,(3) this discrepancy is probably due to the difference in the solubilities of calcium carbonate and strontium carbonate. Since these determinations were both made spectroscopically, the present author attempted a gravimetric analysis of the element. The separation of this small amount of strontium from calcium is, of course, a rather difficult task. R. Fresenius' method(4) of separation, in which the nitrate of both elements are swirled in a mixture of alcohol and ether, was adopted. Since calcium nitrate is about 160 times more soluble than strontium nitrate in a mixture of equal volumes of absolute alcohol and absolute ether, strontium nitrate remains insoluble. 1000 c.c. of sea water, to which ammonium chloride containing little ammonia had been added, was heated to boiling and a sufficient quantity of ammonium oxalate was poured to precipitate calcium and strontium completely. The filtrate was examined if any calcium was present. The precipitation was repeated several times in order to remove magnesium as completely as possible. The oxalates of calcium and strontium were converted by ignition into oxides, and then dissolved in dilute nitric acid, evaporated to dryness on a water bath and finally dried completely in an air bath at above 130°C. The procedure of separation, hereafter, was carried on with alcohol and ether according to the direction of Hillebrand and Lundell. The separation was repeated twice and a very small quantity of undissolved strontium nitrate was filtered off on a small filter paper and ignited to a constant weight.

From this gravimetrical result, the content of strontium in the sea water of the Pacific Ocean near Japan has been found to be 14.4 mg. per

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* Part 1: this volume, 29.

(1) A. Desgrez and J. Meunier, *Compt. rend.*, **183** (1926), 689.

(2) *Bull. Nat. Research Council*, **85** (1932), 95.

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

(4) Hillebrand and Lundell, "Applied Inorganic Analysis," 490, New York (1929).

litre, which is almost of the same order in amount in values as the results from the spectroscopic method. The slight difference between the two methods is unavoidable because of the inherent difficulties of the analytical processes.

Boron. After the geochemical studies of boron had been published by V. M. Goldschmidt and Cl. Peters,(5) the boric acid content in sea water became one of the most interesting subject in oceanographical chemistry. V. M. Goldschmidt and his collaborator determined precisely the boron content in various earth crust forming materials by the spectroscopic method. Thereby, they obtained the result that sea water contains 30 mg. of B_2O_3 per litre, a value considerably larger than L. Dieulafait's(6) old data. According to L. Dieulafait's determination, which is frequently referred to in text-books of oceanography, the quantity of boron in sea water has been estimated to be at least 0.2 mg. per litre. As H. Wattenberg(3) stated in his recent paper, this is one of the few cases, where the older analyses gave a value too low for the rarer elements in the sea water.

Immediately after the investigation of Goldschmidt and Peters, H. Wattenberg(7) tried to ascertain the boric acid content in sea water by the direct titration method, using mannitol and a sodium hydroxide solution. He obtained by this method quite easily 15.6 mg. and 16.1 mg. of B_2O_3 per litre, which are in good agreement in the order of the magnitude with Goldschmidt's value. At the same time, independently of H. Wattenberg, E. G. Moberg and M. W. Harding(8) of the Scripps Institute obtained almost the same result. If these higher values are correct, then besides carbonic acid, boric acid must be taken into consideration in the acid-base equilibrium in sea water. So K. Buch,(9) using the data of the above mentioned authors and the one obtained by himself, calculated theoretically the influence of the boric acid upon the pH value of sea water; at the same time, he gave the chlorinity ratio of boron in sea water, which seemed to be almost constant and expressible by the following formula:

$$B‰ = 0.00023 \sim 0.00025 \times Cl‰$$

Now, an attempt was made to determine the boric acid content in waters of the Pacific Ocean near Japan by the gravimetric methods inasmuch as all of the former values had been obtained either spectrographically or volumetrically.

At first Gooch and Jones' method has been tried. It determines boron gravimetrically as calcium borate, after the extraction of the borate with ethyl alcohol and expelling it as a methyl ester. A 1000 c.c. portion of sea water, was evaporated to dryness, and then methyl alcohol was added, followed by an extraction overnight.

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(5) V.M. Goldschmidt and Cl. Peters, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1932**, 402, 528.

(6) L. Dieulafait, *Compt. rend.*, **85** (1877), 1352.

(7) H. Wattenberg, "Wiss. Ergeb. Meteor-Exp.," VIII, 132, Berlin (1933).

(8) E.G. Moberg and M.W. Harding, *Science*, **77** (1933), 510.

(9) K. Buch, *J. conseil intern. exploration mer*, **8** (1933), 309.

With all the scrupulous care, the results obtained were always too low, when compared with the former values. By this method, there could not be obtained a value higher than 1.2 mg. of H_3BO_3 per litre. The second method adopted was Chapin's procedure, in which boric acid in sea salt is expelled directly with the vapour of methyl alcohol, thus forming a methyl ester of boric acid, which is converted to calcium borate. As by Jones and Gooch's method, values so high as the titrimetric ones could not be obtained by this method. The maximum value was 7.3 mg. of H_3BO_3 per litre.

In both of these cases, the chief sources of failure lay probably in the difficulty in extracting or expelling the small amount of boric acid from so large a bulk of other salts. After several trials had been in vain, the original plan of gravimetric determination was given up and the method of direct titration of sea water was adopted by modifying H. Wattenberg's procedure at a few points.

To a 100 c.c. portion of sea water, a slight excess of hydrochloric acid solution was added and after heating under suction to remove carbon dioxide completely, the excess of hydrochloric acid was cautiously titrated with a solution of sodium hydroxide using *p*-nitrophenol as the indicator. Then a small quantity of mannitol was added to produce free acid which was titrated with a 0.1 or 0.05 N solution of sodium hydroxide (the indicator, phenolphthalein).

Also invert sugar was used in place of mannitol, as recommended by I. M. Kolthoff.(10) The values of both procedures were in good agreement with those of Wattenberg and others. The results are given in Table 1.

Table 1.

Position		Chlorinity	B (mg./l.)	B (‰)/Cl (‰)
Lat. N	Long. E			
36°14′	141°26′	19.24	4.73	0.000246
38°22′	142°35′	18.76	4.73	0.000252

The chlorinity ratios of boron here obtained were almost the same as the upper limit of the values calculated by K. Buch. To eliminate the influences of other salts, known quantities of boric acid were added to the sea water and titrated as usual, the results were completely additive. Recently I. Igelsrud, T. G. Thompson, and B. M. G. Zwicker(11) determined the boron content in sea water on 377 samples from the coastal waters of the Northeastern Pacific. They obtained the result that the average boron-chlorinity ratio is 0.0223 (this is not the ratio of the number of promille boron to the chlorinity as described above, but the value milligram atom boron divided by the chlorinity). When compared with this average, the boron-chlorinity ratio obtained by the author seems to be

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(10) I.M. Kolthoff, "Die Massanalyse," 119, Berlin (1928).

(11) I. Igelsrud, T.G. Thompson, and B.M.G. Zwicker, *Am. J. Sci.*, [5], **35** (1938), 47.

slightly larger (0.0228, 0.0234). A further quantitative discussion will be done in future.

Summary.

(1) Strontium in sea water from the Western Pacific Ocean has been determined gravimetrically; the analytical result: 14.4 mg. Sr per litre.

(2) Boron in sea water has been determined volumetrically; the analytical result: 4.73 mg. B per litre.

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