THE BROMINE-CHLORINITY RATIO OF SEA WATER

By

THOMAS G. THOMPSON AND EDWIN KORPI

Chemical and Oceanographic Laboratories
University of Washington, Seattle

Dittmar (3) first showed that a constant ratio apparently exists between the bromides and the total halides in the waters of the several oceans. Some years later Winkler (13) determined the bromine in samples of sea water, and the bromine-chlorinity ratio calculated from his results showed remarkable agreement but were slightly higher than those of Dittmar. The ratio was obtained from the expression

$$\frac{\text{Grams Br per kilo}}{‰\ \text{Cl}} = K$$

where ‰ Cl is the chlorinity of the sea water, defined until recently as the total weight in grams of halides calculated as chlorides in a kilogram of sea water.

The bromine content of sea water was determined by Dittmar using a method of fractional precipitation while Winkler oxidized the bromides and aspirated the liberated bromine. The former's value for K was 0.0034_1 and the latter's, 0.0034_7. Thus the establishment of the constancy of this ratio permits the estimation of bromine in sea water from the chlorinity by a simple calculation for practical purposes.

In recent investigations in the Japan Sea, Vasil'ev (12) reported that the bromine content of these waters was about 2 mg. less per kilogram of sea water than expected from the ratio of Winkler and Dittmar. On the other hand, Ratmanoff (9) showed that the waters of Bering Strait and Bering Sea were considerably higher in concentrations of bromine than those of the Pacific. Using his own data and those of Vasil'ev, he demonstrated that the bromine-chlorinity ratio decreases with a decrease in latitude. From studies made by one of us of the circulation of waters of the Northeast Pacific and Bering Sea, the conclusions of Vasil'ev and Ratmanoff were doubted. Recently Miyake (8) has investigated the bromine content of waters of the western Pacific and obtained a ratio approximating that of Dittmar and Winkler. However he used the colorimetric method of Dibdin and Cooper (2) which he claimed may not be as accurate as other methods.

In view of the above it was decided to make a study of the bromine content of waters of the Northeast Pacific, Bering Sea, and Bering Strait.

SOURCES OF SAMPLES STUDIED

The authors collected a number of samples at different depths and localities in Bering Strait and Bering Sea from the U. S. Coast Guard Cutter *Northland* and in the Northeast Pacific and Puget Sound regions from the University of Washington research ship *Catalyst* (11). All samples were secured with the Nansen-Knudsen bottles equipped with standard protected reversing thermometers. Samples of water from the Antarctic Ocean were secured by the British-Australian-New Zealand Antarctic Research Expedition, the chlorinities being determined by A. Howard, chemist of the expedition, and checked later by the authors.

METHODS OF ANALYSIS

Chlorinity. The chlorinity was determined by titration with silver nitrate solution using potassium chromate as an indicator (10). The silver nitrate solution was standardized against the standard sea water supplied by the Hydrographical Laboratories of Copenhagen.

Chlorinity of the standard water of Copenhagen is based upon the atomic weights of 1901 and by international agreement is used for all oceanographic investigations as a basis of chlorinity and salinity determinations. (It should not be used as a standard for other constituents of sea water.) Jacobsen and Knudsen (4) have shown that 58.99428 grams of atomic weight silver prepared especially by Otto Hönigschmid is equivalent to 19.3809 grams of chloride of the standard water. Chlorinity is now defined in respect to a unit weight of silver thus insuring a constancy of comparison of sea water throughout the world and independent of changes in atomic weight. A solution of sodium chloride containing 35.457 grams of chloride per kilogram of solution has a chlorinity of 35.441.

In the determination of the chlorinities reported here the maximum variation between extremes was 0.012‰ Cl with an average variation of $\pm$0.004‰ Cl.

Bromine. The van der Meulen method described by Kolthoff and Yutzy (6) gave excellent results using sodium formate solution to reduce the excess of hypochlorite instead of hydrogen peroxide. The standard solutions required for the determination were prepared as follows:

Standard Potassium Bromide: 11.902 grams of pure potassium bromide free of chloride and prepared by thermal decomposition of pure potassium bromate were dissolved and diluted in a liter volumetric flask. 100 ml. of this solution were pipetted and diluted to exactly one liter, and aliquots of this were used for standardizing the thiosulfate solution as described below. The actual molarity of the bromide solution was ascertained by taking aliquots, precipitating AgBr with a slight excess of silver nitrate, and weighing the precipitate.

Standard Sodium Thiosulfate Solution: 5 grams $Na_2S_2O_3 \cdot 5H_2O$ were dissolved in freshly boiled distilled water to give a volume of 2 liters. A few drops of CS_2 were placed in the solution to stabilize it. The solution was standardized as follows: 10 ml. of standard 0.0100 M potassium bromide solution were pipetted into a 600 ml. Erlenmeyer flask and diluted to 100 ml. 10 ml. NaH_2PO_4 solution were introduced and then 5 ml. NaOCl solution. The solution was then heated and boiled. When partially cooled, 5 ml. $H \cdot COONa$ solution were added. If the latter is introduced while the solution containing the excess hypochlorite is near the boiling point, the sudden evolution of CO_2 may give low results. After decomposition of the excess of hypochlorite, the solution was cooled and 10 ml. 6N H_2SO_4 were poured into the flask. 10 ml. of KI solution were then added and a drop of ammonium molybdate solution to catalyze the reaction between the bromate and the iodide ions. The liberated iodine was titrated with $Na_2S_2O_3$ using starch as an indicator and finally the normality of the solution calculated. Blank determinations were essential.

Determination of bromine in sea water was made by taking 100 ml. sample at 20° C. and treating it with the various reagents as described above. The excess hydroxide in the hypochlorite reagent caused precipitation of magnesium hydroxide and thus care was necessary to prevent bumping on boiling. The liberated iodine was titrated and the bromine content per liter of sea water calculated. From the chlorinity of sea water the density of each sample at 20° C. was ascertained from Knudsen's Hydrographical Tables (5), and the bromine content per kilogram of sea water was determined.

The method was found to be very reliable; the average variation between duplicates on 151 samples was about 0.25%.

DISCUSSION OF DATA

In Table I are given the temperatures *in situ*, chlorinities, grams of bromine per kilogram of sample, and the bromine-chlorinity ratios for waters secured from Bering Strait and northern Bering Sea. Much of this area is very shallow, and seldom do depths as great as 50 meters occur. A current flows continually in a general northerly direction from Bering Sea through Bering Strait into Chukchi Sea. The velocity of this current may be decreased or increased by wind and during the winter influenced by ice. Table II contains similar data for the southern portion of Bering Sea, the samples having been taken in the vicinity of the Pribilof Islands and about 500 miles south of Bering Strait.

In cruising from Dutch Harbor to the Strait of Juan de Fuca surface samples were obtained hourly. Many of the samples taken in the Pacific in the area about 1000 miles east of Dutch Harbor and 250 miles west of the Strait of Juan de Fuca were analyzed for bromine. These data are given in Table III.

Two stations for water sampling were occupied beyond the continental shelf off the coast of the State of Washington, and samples were secured at various depths. Data from these two stations are given in Tables IV and V. Samples were likewise taken from various depths in the Strait of Juan de Fuca and at the entrance to Admiralty Inlet, Puget Sound, and the data are given in Tables VI and VII.

In Table VIII are given the results of determinations made on waters from the Antarctic Ocean. Because of the limited volume of samples available, 50 ml. of sea water were used instead of 100 ml.

For all the samples reported above, an average ratio of 0.0034_7 was obtained. Extremes of experimental errors could cause the ratio to vary from 0.0034_4 to 0.0035_1. However for the particular methods used, the average deviation from the mean should be less than ± 0.00002. The data show remarkable constancy for the bromine-chlorinity ratio but are not in agreement with observations and conclusions of Vasil'ev (12) and Ratmanoff (9). It is believed that this discrepancy is due to experimental errors of their method for determination of bromine. (The method of Deniges and Chelle (1) was used by them after a study of other procedures.)

Samples from the Antarctic gave an average bromine-chlorinity ratio that was slightly lower than that for northern waters. These samples were collected from eight to ten years prior to the others investigated, but they had been carefully stored in the original containers, doubly sealed, until analysis in 1940.

Lyman and Fleming (7) give Dittmar's ratio, corrected for atomic weights, as 0.00340. This value has been generally accepted. Dittmar's ratio published in 1884 for the oceans of the world is slightly less than that reported above while that of Winkler's for a limited number of samples is in much better agreement. Ratios calculated from data of other investigators vary from 0.0029 to 0.0044 but much of these data resulted from using methods of questionable or insufficient accuracy. Very decided variations are reported by individual investigators. Thus the 55 samples analyzed by Vasil'ev and Ratmanoff show bromine-chlorinity ratios from 0.0032 to 0.0044 but the average of all of them is 0.0034_5.

Different methods of analysis for bromine will tend to give different results, the variations depending upon the accuracies and precisions of the method and the presence of interfering substances in the samples of sea water. Thus the presence of iodides and iodates would tend to give high results for bromine. These ions occur in sea water (7, 11) but in very small quantities. The iodides if present would be oxidized to iodates which would later react with the potassium iodide introduced during the determination. However the error would be about +0.00001 in the bromine-chlorinity ratio. In like manner any other substances present that would be oxidized by the hypochlorite giving compounds that would eventually liberate iodine from the potassium iodide, would increase the ratio. Bromates do not occur in sea water.

SUMMARY

1. The bromine-chlorinity ratios for waters of Bering Sea and the Northeast Pacific have been determined and found to be remarkably constant.

2. The bromine content of sea water when using the method described may be ascertained readily from the chlorinity of a sea water by multiplying by the factors 0.0034_7 to give the concentration as grams or 0.043_4 as milligram atoms.

TABLE I—Grams Bromine Per Kilo of Sea Water and the Bromine-Chlorinity Ratio Bering Strait and Northern Bering Sea. July 31 and August 1, 1937

Depth Meters	*Temp. °C.*	*Cl °/oo*	*Br °/oo*	*Br/Cl*	*Location*
10	3.91	17.67	0.0613	0.0034_7	Lat. 66° 04′ N., Long. 168° 14′ W.
50	3.04	17.75	.0616	34_7	
0	9.72	17.26	.0606	35_1	Lat. 65° 46′ N., Long. 168° 38′ W.
10	5.98	17.86	.0618	34_6	
0	12.79	15.82	.0551	34_8	Lat. 65° 22′ N., Long. 168° 15′ W.
0	13.58	14.56	.0507	34_8	Lat. 64° 40′ N., Long. 167° 07′ W.
20	2.30	17.16	.0594	34_6	
			Mean	0.0034_7	

TABLE II—GRAMS BROMINE PER KILO OF SEA WATER AND THE BROMINE-CHLORINITY RATIO OFF PRIBILOF ISLANDS, SOUTHEASTERN BERING SEA. LAT. 57° 22′ N., LONG. 170° 02′ W. AND LAT. 57° 14′ N., LONG. 170° 14′ W.
JULY 16, 17, 18, 1937

Depth (*Meters*)	*Temp.* °*C.*	*Cl* °/oo	*Br* °/oo	*Br/Cl*
0	7.22	17.94	0.0624	0.0034_8
10	7.15	17.98	.0626	34_8
0	7.91	17.87	.0622	34_7
10	7.26	18.02	.0627	34_7
0	7.19	17.81	.0620	34_4
10	7.13	17.96	.0625	34_8
0	7.14	17.94	.0624	34_8
10	7.10	17.96	.0625	34_7
0	6.52	17.95	.0625	34_8
30	6.25	17.98	.0626	34_7
50	6.21	18.01	.0627	34_5
			Mean	0.0034_7

TABLE III—GRAMS BROMINE PER KILO OF SEA WATER AND THE BROMINE-CHLORINITY RATIO SURFACE SAMPLES NORTHEAST PACIFIC BEYOND THE COAST OF BRITISH COLUMBIA. SEPTEMBER 24 AND 25, 1938

Temp. °*C.*	*Cl* °/oo	*Br* °/oo	*Br/Cl*	*Location*	
12.7	17.97	0.0627	0.0034_9	Lat. 52° 06′ N,	Long. 139° 36′ W.
13.6	18.01	.0628	34_9	51° 55′ N.	138° 28′ W.
13.7	18.01	.0623	34_6	51° 52′ N.	138° 11′ W.
13.7	17.97	.0627	34_9	51° 47′ N.	138° 37′ W.
14.0	17.94	.0626	34_9	51° 44′ N.	138° 20′ W.
14.2	17.95	.0623	34_7	51° 41′ N.	138° 03′ W.
14.0	17.95	.0623	34_7	51° 38′ N.	136° 46′ W.
14.0	17.95	.0626	34_9	51° 42′ N.	136° 31′ W.
14.1	17.97	.0627	34_9	51° 32′ N.	136° 01′ W.
14.0	17.98	.0626	34_8	51° 28′ N.	135° 46′ W.
13.9	17.99	.0626	34_8	51° 24′ N.	135° 31′ W.
13.8	17.99	.0626	34_8	51° 20′ N.	135° 16′ W.
14.1	18.00	.0626	34_8	51° 16′ N.	135° 01′ W.
14.0	17.99	.0621	34_5	51° 12′ N.	134° 43′ W.
14.4	17.92	.0624	34_8	51° 08′ N.	134° 27′ W.
14.7	17.97	.0624	34_7	51° 04′ N.	134° 11′ W.
14.7	17.96	.0623	34_7	51° 00′ N.	134° 55′ W.
14.8	17.97	.0625	34_8	50° 36′ N.	133° 39′ W.
14.9	17.97	.0627	34_9	50° 52′ N.	133° 23′ W.
13.1	17.98	.0628	34_9	50° 37′ N.	132° 33′ W.
		Mean	0.0034_8		

TABLE IV—Grams Bromine Per Kilo of Sea Water and the Bromine-Chlorinity Ratio Northeast Pacific Ocean, off Coast of State of Washington. Lat. 47° 19′ N., Long. 125° 10′ W. July 8, 1939. Depth 1171 Meters

Depth (*Meters*)	*Temp.* °*C.*	*Cl* °/oo	*Br* °/oo	*Br/Cl*
0	15.23	17.81	0.0618	0.0034_7
10	14.66	17.83	.0617	34_6
20	11.94	17.87	.0626	35_0
30	9.03	17.98	.0627	34_8
50	8.02	18.06	.0630	34_8
75	7.70	18.29	.0631	34_6
100	7.64	18.54	.0637	34_4
200	7.58	18.78	...	..
300	5.89	18.84	.0657	34_9
400	5.54	18.87	.0654	34_6
500	5.04	18.89	.0660	34_9
600	4.58	18.92	.0661	34_9
700	4.28	18.97	.0662	34_9
800	4.00	19.00	.0662	34_8
900	3.82	19.01	.0662	34_8
			Mean	0.0034_7

TABLE V—Grams Bromine Per Kilo of Sea Water and the Bromine-Chlorinity Ratio Northeast Pacific Ocean, off Coast of State of Washington. Lat. 47° 09′ N., Long. 125° 10′ W. July 8, 1939. Depth 1427 Meters

Depth (*Meters*)	*Temp.* °*C.*	*Cl* °/oo	*Br* °/oo	*Br/Cl*
0	15.04	17.72	0.0617	0.0034_8
10	14.60	17.74	...	..
20	12.10	17.87	.0622	34_8
30	9.61	17.98	.0629	35_0
50	8.18	18.06	.0629	34_8
75	8.00	18.22	...	..
100	7.89	18.49	.0643	34_8
200	6.49	18.78	.0661	35_2
500	5.75	18.83	.0651	34_6
800	4.92	18.89	.0650	34_4
900	4.47	18.92	.0663	35_0
1000	4.26	18.96	.0662	34_9
1100	4.04	18.98	.0664	35_0
1200	3.76	19.01	.0664	34_9
1300	3.50	19.03	.0666	35_0
1400	3.35	19.05	.0667	35_0
			Mean	0.0034_8

TABLE VI—Grams Bromine Per Kilo of Sea Water and the Bromine-Chlorinity Ratio Strait of Juan de Fuca. Lat. 48° 182′ N., Long. 124° 03.1′ W. January 14, 1939

Depth (*Meters*)	*Temp.* °*C.*	*Cl* °/oo	*Br* °/oo	*Br*/*Cl*
0	7.94	17.28	0.0605	0.0035_0
10	7.99	17.31	.0601	34_7
20	7.93	17.34	.0607	35_0
30	7.93	17.35	.0609	35_1
50	7.83	17.55	.0611	34_8
75	7.73	17.75	.0619	34_9
100	8.21	18.24	.0636	34_9
180	8.28	18.62	.0648	34_8
			Mean	0.0034_9

TABLE VII—Grams Bromine Per Kilo of Sea Water and the Bromine-Chlorinity Ratio Waters of Puget Sound. January 13, 1939

Depth (*Meters*)	*Temp.* °*C.*	*Cl* °/oo	*Br* °/oo	*Br*/*Cl*	*Location*
0	8.26	16.48	0.0570	0.0034_6	Point No Point
10	8.47	16.60	.0573	34_5	Lat. 47° 54′ N., Long. 122° 28.7′ W.
20	8.37	16.64	.0579	34_8	
30	8.39	16.66	.0580	34_8	
50	8.36	16.69	.0581	34_8	
75	8.48	16.74	.0583	34_8	
100	. .	16.77	.0582	34_7	
150	8.72	16.83	.0584	34_7	
200	8.72	16.84	.0586	34_8	
			Mean	0.0034_7	
0	8.12	16.43	0.0572	0.0034_3	Off Port Townsend
10	8.13	16.50	.0574	34_8	Lat. 48° 08′ N., Long. 122° 41.1′ W.
20	8.11	16.60	.0578	34_8	
30	8.16	16.68	.0577	34_6	
50	8.02	16.83	.0587	34_9	
75	7.99	16.85	.0588	34_9	
100	8.01	16.90	.0590	34_9	
			Mean	0.0034_8	

TABLE VIII—Grams Bromine Per Kilo of Sea Water and the Bromine-Chlorinity Ratio Various Locations in the Antarctic Ocean, Surface Waters November and December, 1930

*Cl** °/oo	*Br* °/oo	*Br*/*Cl*	*Location*	
19.04	0.0655	0.0034_4	Lat. 47° 20′ S.	Long. 146° 25′ E.
18.86	.0654	34_7	50° 56′ S.	147° 08′ E.
18.85	.0658	34_9	52° 25′ S.	153° 21′ E.
18.83	.0648	34_4	53° 04′ S.	154° 51′ E.
18.76	.0643	34_3	55° 55′ S.	158° 42′ E.
18.75	.0641	34_2	58° 14′ S.	160° 40′ E.
18.83	.0646	34_3	59° 16′ S.	160° 57′ E.
18.77	.0648	34_5	63° 07′ S.	166° 55′ E.
18.77	.0648	34_5	51° 06′ S.	104° 25′ E.
	Mean	0.0034_5		

* Determined by Mr. A. Howard, chemist for the British-Australian-New Zealand Antarctic Research Expedition.

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