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# COMPOSITION OF SEA WATER\*

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The principle of constant ratios between the salts in ocean water unaffected by land drainage was laid down by Forchhammer in 1864, and firmly established by Dittmar (1884). Dittmar's examination of 77 samples, collected from all the oceans of the world by H.M.S. *Challenger* in 1873-76, was so comprehensive, and his results so consistent, that some of his values are used to this day. Most estimates of the composition of sea water are based fundamentally on Dittmar's work, since subsequent individual investigations have usually been restricted to the determination of one or a few of the major constituents and the establishment of the ratios of these constituents to the chlorinity. In view of the number of such values now available it was considered of interest to prepare a revised table for the composition of ocean water. Also the more accurate methods of analysis now in use make it possible to consider the composition with greater detail. As Dittmar's values have formed the basis of such estimates, it is necessary to consider the effect on his original results of the use of more nearly exact values for atomic weights.

In order to recalculate Dittmar's values with the present accepted atomic weights, the methods by which the various constituents were determined must be taken into account. It is of course implied that the analytical methods were in themselves accurate. Table I compares the atomic weights used by Dittmar with the 1939 International values (Baxter *et al.*, 1939). In the case of potassium, Dittmar used two different values, 39 when computing the results of potassium determinations, and 39.13 when weighing KCl as a standard for chloride titrations. Table II gives the percentage composition of the salts in sea water as reported by Dittmar (1884, p. 203), the factors by which they were calculated from his weighings, and the result of recalculating these percentages with 1939 atomic weights. Dittmar's

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values for calcium oxide and bromine were obtained, not from the entire 77 samples, but from three composite *Challenger* samples and a fourth sample collected near Arran, Scotland. Furthermore, it should be pointed out that sodium was not determined directly, but was estimated by summing the equivalents and calculating the sodium from the deficiency of basic constituents below acidic constituents. Hence any change in the other constituents automatically changes the amount of sodium. Dittmar does not state how he standardized the HCl used in his carbonic acid determinations, but the amount is

TABLE I  
COMPARISON OF ATOMIC WEIGHTS

	<i>Dittmar, 1884</i>	<i>International, 1939</i>
<i>Ag</i>	107.93	107.880
<i>Ba</i>	137	137.36
<i>Br</i>	79.95	79.916
<i>C</i>	12	12.010
<i>Ca</i>	40	40.08
<i>Cl</i>	35.46	35.457
<i>K</i>	39	39.096
<i>and</i>	39.13	
<i>Mg</i>	24	24.32
<i>Na</i>	23	22.997
<i>O</i>	16	16.0000
<i>P</i>	31	30.98
<i>Pt</i>	198	195.23
<i>S</i>	32	32.06

so small that revised atomic weights would introduce a negligible correction.

A complete analysis of water, for those constituents which bear a virtually constant ratio to the total salt, can be obtained from determination of a single one of these components. It is convenient to refer to these as the *major constituents* of sea water. The major constituent most easy to determine accurately is the silver-precipitating halides, and for this reason the other elements are expressed as a function of chlorinity. Chlorinity, as defined by Knudsen (1902), was the weight in grams (*in vacuo*) of the chlorides contained in one kilogram of sea water (likewise measured *in vacuo*) when all the bromides and iodides have been replaced by chlorides; in other words, the result given directly by the silver nitrate titration. To this definition must be added that the titration results be calculated with the Hydrographical Tables of Knudsen (1901, pp. 23-34) using Copen-

hagen Normal Water as the standard. *It is desirable to maintain an unvarying international standard for chlorinity, independent of atomic weights, in order that the apparent chlorinity of the oceans shall not change as revisions in atomic weights change gravimetric factors.* The Normal Water prepared by the Hydrographic Laboratories of Copenhagen has fulfilled this function. As pointed out by Matthews (Deacon, 1933), all batches of Normal Water have been referred to an original KCl primary standard calculated with 1902 atomic weights; that is, chlorinity as originally defined was identical with the volumetric chlorine-equivalent as calculated with 1902 atomic weights.

TABLE II

PERCENTAGE COMPOSITION OF SEA WATER SALTS AS REPORTED BY DITTMAR, AND AS CALCULATED FROM HIS RESULTS USING 1939 ATOMIC WEIGHTS

	<i>Dittmar,</i> 1884	<i>Factor used</i> <i>in calculation</i>	<i>Dittmar, 1939</i> <i>atomic weights</i>
<i>Cl</i>	55.292	Cl/KCl	55.262
<i>Br</i>	0.1884	Br/(Br - Cl)	0.1882
<i>SO<sub>3</sub></i>	6.410	SO <sub>3</sub> /BaSO <sub>4</sub>	6.397
<i>CO<sub>2</sub></i>	0.152	CO <sub>2</sub> /HCl · HCl/x	0.152
<i>CaO</i>	1.676	weighed directly	1.674
<i>MgO</i>	6.209	MgO/Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	6.237
<i>K<sub>2</sub>O</i>	1.332	K <sub>2</sub> O/Pt	1.353
<i>Na<sub>2</sub>O</i>	41.234	by difference	41.224
	112.4934	Sum	112.4872
	12.4934	oxygen-equivalent of halide	12.4872

Jacobsen and Knudsen (1940) have established a permanent standard for chlorinity identical with the previous one but independent of the store of Normal Water at Copenhagen. The mass of silver required to precipitate completely the halogen in one kilogram of Normal Water of  $19.381 \pm 0.001\%$  chlorinity was found to be  $58.9943 \pm 0.0008$  grams. The new definition of chlorinity is expressed by  $\text{Cl} \% = 19.381/58.9943 = 0.3285234 \text{ Ag} \%.$  The 1939 atomic weight ratio Cl/Ag is  $35.457/107.880$  or  $0.328671.$  Thus the chlorine-equivalent, based on 1939 atomic weights, is  $1.00045 \text{ Cl} \%.$  For Copenhagen Normal Water labelled  $19.384\%$  the chlorine equivalent would be  $19.393$  grams per kilogram. Deacon (1933), as calculated by Matthews, actually found  $19.394$  as the chlorine-equivalent of such a water, using NaCl as a primary standard, while Thompson and Wirth (1931) found in the same way  $19.378$  for a water labelled  $19.368\%$  chlorinity.

Table III compares the ratios to chlorinity of the other constituents in sea water of 19.000 ‰ chlorinity as calculated from Dittmar's results in the manner previously explained, with the best values of more recent investigations. The chlorinity in each case has been adjusted to that of Copenhagen Normal Water.

TABLE III

COMPARISON OF DITTMAR'S RATIOS WITH PRESENT BEST VALUES, AND  
COMPOSITION OF SEA WATER HAVING CHLORINITY 19.000‰

<i>Ion</i>	<i>Ratio to chlorinity (Dittmar)</i>	<i>Ratio to chlorinity (best value)</i>	<i>Authority</i>	<i>Equivalents per kilogram</i>	<i>Weights per kilogram</i>
<i>Cl</i>	0.99894	0.99894	Dittmar (1884) and Jacobsen and Knudsen (1940)	0.53529	18.9799
<i>Br</i>	.00340	.00340	Dittmar (1884)	.00081	.0646
<i>SO<sub>4</sub></i>	.1388	.1394	Thompson, Johnston and Wirth (1931)	.05514	2.6486
<i>HCO<sub>3</sub></i>	.00760	.00735	Revelle (1936)	.00229	.1397
<i>F</i>	—	$7 \times 10^{-5}$	Thompson and Taylor (1933)	.00007	.0013
				0.59360	
<i>Ca</i>	.02163 <sup>1</sup>	.02106	Kirk and Moberg (1933) and Thompson and Wright (1930)	.01996	.4001
<i>Mg</i>	.06801	.06695	Thompson and Wright (1930)	.10460	1.2720
<i>K</i>	.02029	.02000	Thompson and Robinson (1932)	.00972	.3800
<i>Sr</i>	—	.000702	Webb (1938)	.00030	.0133
				0.13458	
<i>Na</i>	.5530	.5556	By difference	.45902	10.5561
				0.59360	
<i>H<sub>3</sub>BO<sub>3</sub></i>	—	.00137	Harding and Moberg (1933) and Igelsrud, Thompson and Zwicker (1938)		.0260
					34.4816

<sup>1</sup> This ratio of Dittmar's is for calcium plus strontium, determined gravimetrically as oxide. The calcium and strontium best values would be 0.02165 if calculated on this basis.

The ratios for chlorine to chlorinity and bromine to chlorinity have been calculated from Dittmar's bromine : chlorinity ratio, and from the factor 1.00045 just derived. At 19.000 ‰ chlorinity, we obtain 18.9799 grams of chlorine and 0.0646 grams of bromine per kilogram. This bromine is equivalent to  $0.0646 \times 35.457/79.916 = 0.0287$  grams

of chlorine, so the total chlorine-equivalent is 19.0086 and the ratio to chlorinity  $19.0086/19.0000 = 1.00045$ .

In order to make it possible to consider the sum of all the constituents of sea water, some of the ratios of other constituents to chlorinity have been carried to a number of figures probably not justified by the accuracy of the procedures by which they were determined. In the following discussion, unless otherwise stated, the units used are grams per kilogram of sea water.

The sulfate : chlorinity ratio for a series of samples from various oceans was found by Thompson, Johnston and Wirth (1931) to be 0.1395; corrected for buoyancy in weighing, this is 0.1394. Revelle (1936) found as the base ratio for surface sea water of the northeast Pacific 0.1235 m.eq./liter per Cl ‰. Using a mean density of 1.025 and assuming all the base to be in the form of bicarbonate, we obtain a weight ratio  $\text{HCO}_3/\text{Cl} = 0.0735$ . Fluorine in sea water was determined by Thompson and Taylor (1933), who found fluorine : chlorinity  $= 7 \times 10^{-5}$ .

Thompson and Wright (1930) found 0.02150 gravimetrically for the calcium : chlorinity ratio for water of the northeast Pacific. Corrections for the buoyancy in weighings, a slight revision in the atomic weight of calcium, and the fact that NaCl was used as a primary Cl standard, cancel almost exactly. Kirk and Moberg (1933) found 0.02154 volumetrically for water of the same region, and here again, changes in atomic weights of carbon and calcium cancel. Webb (1938), however, has pointed out that strontium in sea water is chemically indistinguishable from calcium, and leads to a high value for the apparent calcium. With a calcium : strontium ratio of 30 : 1 (Desgrez and Meunier, 1926; Thomas and Thompson, 1932), these calcium : chlorinity ratios become respectively 0.02090 and .02122, their mean 0.02106, and the mean strontium : chlorinity ratio, 0.000702.

A magnesium : chlorinity ratio of 0.06694 is reported by Thompson and Wright (1930). This is subject to the same buoyancy and chlorinity corrections as their calcium ratio and furthermore to a change in the gravimetric factor resulting from a revision in the atomic weight of phosphorus, becoming finally 0.06695. Potassium is extremely difficult to determine in sea water. Potassium : chlorinity  $= 0.02000$  was obtained by Thompson and Robinson (1932, p. 68) as an average of the values in the literature up to their time, and the recent result of Webb (1939) of  $0.02009 \pm 0.00020$  is in good agreement with this. For sodium we prefer to follow Dittmar and calculate sodium as the deficiency of the other positive ions below the negative ions. The result yielded by this method, sodium : chlorinity  $= 0.5558$ , compares

well with the recent value of Webb (1939) from direct analysis, 0.5549  $\pm$  0.0010, and is somewhat higher than the average given by Thompson and Robinson (1932, p. 174) of 0.5509.

Boric acid, which we assume not to be ionized in sea water to any appreciable extent, has been determined by Harding and Moberg (1933) and Igelsrud, Thompson and Zwicker (1938). The former found boron : chlorinity = 0.000239 by weight; the latter 0.0223 mg.at./unit Cl ‰, which is 0.000241 by weight; the mean, 0.000240 is equivalent to a boric acid : chlorinity ratio of 0.00137.

Several analyses of north Pacific sea water have recently appeared (Wentworth, 1939; Miyake, 1939). Lack of sufficient information as to the methods of analysis makes it difficult to evaluate the accuracy of these determinations, and we accordingly have not included them in preparing Table III.

The sum of all the major constituents in sea water of 19.000‰ chlorinity will now be considered. Knudsen (1902) defined salinity as the weight in grams (*in vacuo*) of the solids that can be obtained from one kilogram of sea water (likewise measured *in vacuo*), when all the bromides and iodides are converted to chlorides, the carbonates to oxides, and the remainder dried at 480° to constant weight. If we take the values given in Table III and convert the bromide to chloride and the bicarbonate to oxide (Table IV), we arrive at a value of 34.3243 for salinity, as compared with 34.325 derived from Knudsen's equation given below.

TABLE IV  
CALCULATION OF SALINITY

0.1397	HCO <sub>3</sub> = 0.0183	O	Total salt	34.4816
.0646	Br = .0287	Cl		.1573
<hr/>				<hr/>
0.2043	0.0470		Salinity	34.3243
.0470			Salinity from Knudsen's Tables	34.325
<hr/>				<hr/>
0.1573				

It should be emphasized that the ratios just presented hold good only at chlorinities near 19.00 ‰. Knudsen (1901) in fitting a straight line to his nine direct salinity : chlorinity determinations, obtained the expression  $S \text{ ‰} = 0.030 + 1.8050 \text{ Cl ‰}$ , which implies that water having a negligible chlorinity still contains carbonates (expressed as oxides) and sulfates to the extent of 0.030 ‰. Hence the ratios of the major constituents to chlorinity depend on chlorinity. An explanation for this is easily found in the well-known observation

that river water contains more carbonate than sulfate and more sulfate than chloride. Since river water likewise contains more calcium than magnesium, and more magnesium than sodium or potassium, it would be expected that the ratios of carbonate, sulfate, calcium and magnesium to chlorinity all increase with decreasing chlorinity.

This has been shown to be true in the case of carbonate by Mitchell and Solinger (1934), but their ratios at low chlorinities are extremely variable. For the sulfate data from the Baltic, corrected for buoyancy, of Thompson, Johnston and Wirth (1931), the method of least squares yields a straight line,  $SO_4 = 0.0061 + 0.1391 \text{ Cl } \%$ . There are no data for magnesium which can be used in this way. For calcium, Gripenberg (1937) has some very interesting results from the Baltic. She shows that four separate water masses can be distinguished in this area on the basis of their calcium : chlorinity relationships. These yield four straight lines for calcium as a function of chlorinity, the constant term ranging from 0.0019 to 0.0226 and the slope from 0.0258 to 0.0204. The two Baltic stations used by Knudsen to determine the chlorinity : salinity relationship are located near some of

TABLE V

CALCULATION OF THE COMPOSITION OF THE AVERAGE BALTIC WATER WITH WHICH THE SEA WATER OF KNUDSEN'S TABLES IS DILUTED

$$S = 0.030 + 1.8050 \text{ Cl} \quad (\text{Knudsen, 1901})$$

$$SO_4 = 0.0061 + 0.1391 \text{ Cl} \quad (\text{after Thompson, Johnston and Wirth, 1931})$$

$$Ca = 0.0154 + 0.02025 \text{ Cl} \quad (\text{after Gripenberg, 1937})$$

$$Mg/24.32 + .0154/40.08 = O/16 + .0061/96.06 \dots\dots\dots (1)$$

$$Mg + 0.0154 + O + .0061 = 0.0300 \dots\dots\dots (2)$$

Mg	0.0020	Mg	0.0020	Mg	0.0020	CaCO <sub>3</sub>	0.0385
Ca	0.0154	Ca	.0154	Ca	.0154	MgCO <sub>3</sub>	.0017
SO <sub>4</sub>	.0061	SO <sub>4</sub>	.0061	SO <sub>4</sub>	.0061	MgSO <sub>4</sub>	.0076
O	.0065	CO <sub>3</sub>	.0243	HCO <sub>3</sub>	.0493		
0.0300		0.0478		0.0728		0.0478	

$$Mg = 0.0020 + 0.06684 \text{ Cl } \% \dots\dots\dots (3)$$

$$HCO_3 = 0.0493 + 0.004755 \text{ Cl } \% \dots\dots\dots (4)$$

$$\Sigma = 0.073 + 1.8110 \text{ Cl } \% \dots\dots\dots (5)$$

Knudsen's equation gives the limiting concentration of salts other than chlorides as 0.030 ‰, the carbonate being weighed as oxide. Limiting values for SO<sub>4</sub> and Ca were found as described in the text. Two simultaneous equations (1) and (2) are now written, the first ionic, the second stoichiometric. Solution of these gives the limiting values for Mg and HCO<sub>3</sub>, from which in turn are found (3), (4) and (5).



Gripenberg's stations, and by using her calcium values for these and the ratio already given for 19.000 ‰ chlorinity, the equation  $Ca = 0.0154 + 0.02025 Cl \text{ ‰}$  can be derived. We are now in a position to calculate the corresponding equations for magnesium and bicarbonate. (Table V).

Having these equations, we can calculate the composition of sea water corresponding to that in Knudsen's *Hydrographical Tables* at any chlorinity, assuming that the ratios to chlorinity of all the other components except these four are constants; an assumption which, even if incorrect, will introduce no significant discrepancy. The total salt per kilogram,  $\Sigma$ , as distinguished from the salinity,  $S$ , will be given by the expression,  $\Sigma = 0.073 + 1.8110 Cl \text{ ‰}$ . The total salt per kilogram of solvent water,  $Z$ , will then be  $Z = 1000 \Sigma / 1000 - \Sigma$ , or

$$Z = \frac{73 + 1811 Cl \text{ ‰}}{999.927 - 1.8110 Cl \text{ ‰}}$$

This quantity  $Z$  is useful in dealing with the colligative properties of sea water, as Table VI will show. Here are given the values of  $Z$  corresponding to even units of chlorinity, the freezing point,  $\tau$ , of sea water as measured by Hansen (Knudsen, 1903), and the freezing point as calculated from the equation  $\tau = -0.05241 Z$ . Hansen's attempt to express freezing point as a function of another property of sea water led to a more complicated equation, namely  $\tau = -0.086 - 0.064633 \sigma_0 - 0.0001055 \sigma_0^2$ .

The ionic strength, a quantity of importance in the thermodynamics of solutions, can likewise be calculated for sea water. The ionic strength,  $\mu$ , is computed by first multiplying the concentration of each individual ion, in moles per kilogram of solvent water, by the square of its valence, and then taking half the sum of these products (Lewis and Randall, 1923, p. 373). Proceeding in this way, we obtain

$$\mu = \frac{1.47 + 35.92 Cl \text{ ‰}}{999.927 - 1.8110 Cl \text{ ‰}}$$

which may also be expressed in the form  $\mu = 0.00147 + 0.03592 Cl \text{ ‰} + 0.000068 (Cl \text{ ‰})^2$  in the range of concentrations encountered in naturally occurring sea water. This compares favorably with the equation  $\mu = 0.020 S \text{ ‰} = 0.036 Cl \text{ ‰}$  derived by Buch *et al.* (1932, p. 35) from Dittmar's original analyses.

TABLE VI

TOTAL SALTS PER KILOGRAM OF SOLVENT WATER AND FREEZING POINT

Chlorinity ‰	Z, total salts per kg.H <sub>2</sub> O	$\tau =$ -0.05241 Z	$\tau$ , measured
1	1.888	-0.099	-0.099
2	3.709	.194	.195
3	5.537	.290	.290
4	7.372	.386	.386
5	9.214	.483	.483
6	11.062	.580	.579
7	12.917	.677	.676
8	14.778	.775	.774
9	16.646	.873	.871
10	18.521	.971	.969
11	20.403	1.070	1.068
12	22.292	1.169	1.167
13	24.188	1.268	1.266
14	26.091	1.368	1.366
15	28.001	1.468	1.466
16	29.919	1.568	1.567
17	31.884	1.669	1.668
18	33.778	1.779	1.769
19	35.716	1.872	1.872
20	37.662	1.974	1.974
21	39.616	2.076	2.078
22	41.577	2.179	2.181
23	43.546	-2.283	-2.286

## DISCUSSION

Since chloride determinations made with sodium or potassium chloride as a primary standard, or made gravimetrically, and calculated with the present accepted values for atomic weights, will differ slightly but measurably from determinations using Copenhagen Normal Water, it is important that the method of chloride determination be adequately described in reporting chemical oceanographic data. Variations in the reported ratios of other components to chlorinity may be caused by this ambiguity in the method used for chlorinity. Likewise the ratios must be reduced to a vacuum basis, in accordance with the definitions of salinity and chlorinity.

TABLE VII  
HYPOTHETICAL COMBINATION OF IONS IN SEA WATER

$Cl = 19.00\text{‰}$

<i>Salt</i>	<i>Grams</i>
<i>NaCl</i> .....	23.477
<i>MgCl<sub>2</sub></i> .....	4.981
<i>Na<sub>2</sub>SO<sub>4</sub></i> .....	3.917
<i>CaCl<sub>2</sub></i> .....	1.102
<i>KCl</i> .....	0.664
<i>NaHCO<sub>3</sub></i> .....	.192
<i>KBr</i> .....	.096
<i>H<sub>3</sub>BO<sub>3</sub></i> .....	.026
<i>SrCl<sub>2</sub></i> .....	.024
<i>NaF</i> .....	.003
Sum.....	34.482
<hr/>	
<i>H<sub>2</sub>O</i> to	1000.000

That the ratios of other ions to chlorinity in sea water are not strictly constant follows from the relationship between chlorinity and salinity established by Knudsen. Brackish waters will vary according to the nature of the particular river water with which they are diluted. It happens that water from the Baltic region was selected as the standard type of diluted water in oceanography, and comprehensive tables of its salinity, chlorinity and density relationships worked out. It follows from this that it is not possible, by extrapolation to zero chlorinity of measurements made in natural sea water, to obtain the corresponding property of distilled water, although this has been attempted in the case of refractive index, dissociation constant, and other measurements. It is also incorrect to make electrical measurements in sea water over a range of chlorinity, by diluting a single sample with "a good grade of conductivity water," although this likewise has been done. Samples diluted with distilled water will not correspond in properties to those of water of the same chlorinity from Knudsen's Tables. Furthermore, in any specific locality where dilution by river water occurs water of a given chlorinity will not necessarily have the same properties as water of the same chlorinity obtained by diluting oceanic water with distilled water nor water corresponding to that of Knudsen's Tables.

In Table VII the ions previously presented in Table III are combined as salts. This tabulation may serve as a basic formula for synthetic sea water of chlorinity 19.00 ‰. It should be noted that as only the major constituents have been discussed the so-called plant nutrients and heavy metals are lacking.

Not only must the qualification "in oceanic water unaffected by land drainage" be added to the principle of constant composition of sea salt, but also, the depth at which the sample is obtained must be specified. The nutrient compounds, nitrate, phosphate and silicate, increase with depth to a point where they can no longer be considered infinitesimal, and the decreased pH favors increased solution of  $\text{CaCO}_3$  from settling organic detritus. It was for this reason that the calcium and base ratios presented in Table III were both chosen from determinations on samples taken from the upper layers in the same area.

### SUMMARY

1. Dittmar's values for the composition of the dissolved solids in sea water are recalculated with 1939 atomic weights.

2. If Copenhagen Normal Water is not available, chloride values obtained using a primary Cl standard must be converted to chlorinity. Jacobsen and Knudsen have found the chlorine-equivalent (1939 atomic weights) to be 1.00045 times chlorinity.

3. To correspond to the definitions of chlorinity and salinity, weighings should be corrected to weights *in vacuo*.

4. Modern determinations of the constituent : chlorinity ratios for surface ocean water have been adjusted as given above and compared with Dittmar's values. Since certain of these ratios increase with decreasing chlorinity, the properties of ocean water diluted with distilled water will not agree with Knudsen's Tables. Certain ratios also increase with depth.

5. From these ratios have been calculated a recipe for artificial sea water, and equations for computing total salt per kilogram of sea water,  $\Sigma$ ; total salt per kilogram of solvent water,  $Z$ ; and ionic strength,  $\mu$ ; in terms of chlorinity.

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