

## THE SODIUM AND POTASSIUM CONTENT OF SEA WATER

By D. A. WEBB,<sup>1</sup> Ph.D.

Department of Zoology, Cambridge University

(Received 15 November 1938)

### INTRODUCTION

EVER since the investigations of Forchhammer in the middle of last century it has been known that the composition of sea water throughout the mass of the oceans is relatively constant, and that, whatever be the degree of concentration or dilution, the ratios between the concentrations of the principal components vary, if at all, between narrow limits. Modern workers have not only confirmed this impression, but have shown that in the waters of the open ocean the range of variation of these ionic ratios is so small as to fall well within the experimental error even of the most careful analyses. Only in such specialized regions as the Baltic does the concentration of some of the components, notably calcium when considered in relation to the chlorinity, appear to differ unequivocally from the figures for the open oceans. Even in such cases the difference is remarkably small, amounting to only a very few parts per cent.

It is clearly desirable therefore that authoritative figures should be available for the mean values of the concentrations of these principal components, expressed as fractions of the chlorinity. Such figures would be of value both to the hydrographer and to the physiologist and biochemist, for they would enable the effects of dilution, pollution, etc., to be studied in specialized areas of the sea, and they would render it possible for the experimentalist, investigating problems concerned with the inorganic constituents of tissues and body fluids of marine animals, to obtain by a single titration a complete analysis of the external medium.

Such figures have recently been published by Thompson *et al.* (1931) for the  $\text{SO}_4/\text{Cl}$  ratio, and by Thompson & Wright (1930) for the  $\text{Ca}/\text{Cl}$  and  $\text{Mg}/\text{Cl}$  ratios. For potassium and sodium, however, similar figures are lacking, and in the case of potassium the available estimates by different authors vary widely. The aim of this paper is to attempt to fix more precisely the values of the  $\text{Na}/\text{Cl}$  and  $\text{K}/\text{Cl}$  ratios, both by analysis and by critical discussion of the results of previous authors. The results are far too scanty to make any claim to finality, but it is hoped that they may at least narrow the range within which the true values may be presumed to lie.

Only one sample of water has been analysed, but, once constancy of composition is established, variety in the source of the material would seem to add little to the significance of the results. This sample was collected for me in September 1938 by Dr J. D. Robertson off the south-eastern shore of the Cumbrae in the Firth of

<sup>1</sup> Overseas Scholar of the Royal Commission for the Exhibition of 1851.

Clyde, in a region where no contamination could be suspected. Its chlorinity (18.43 ‰) shows that it cannot have been exposed to any serious degree of dilution by river water. It was stored in a wax-lined bottle and analysed within a few weeks.

The chlorinity, from which both Na/Cl and K/Cl ratios were calculated, was determined by Volhard titration, by gravimetric estimation as silver halides, and by calculation from the specific gravity, according to the data given by Knudsen (1901). The results, expressed as grams Cl per litre, are as follows:

Volhard titration (mean of two)	18.88
Gravimetric (corrected for bromide)	18.87
From specific gravity	18.83
Mean	$18.86 \pm 0.02$

## POTASSIUM

### *Theoretical*

In Table I are summarized the estimates of the K/Cl ratio calculated from the analyses published by various authors since 1880. The figures have been in most cases recalculated from the original data; for a few the summaries given by Clarke (1924) have been used.

Table I

Author	No. of samples	K/Cl
Schmelk (1882)	6	0.02026
Forsberg (1883)	4	0.0211
Dittmar (1884)	77	0.01997*
Natterer (1892-4)	57	0.02011†
Kolotoff (1893)	1	0.0210
Makin (1898)	21‡	0.02004§
Macallum (1903)	3	0.02025
Schloesing (1906)	3	0.01953
Wheeler (1910)	5	0.0263
Steiger   (1910)	1	0.01988
Anderson & Thompson¶	12	0.0191

\* Calculated on the assumption that Pt=198, K=39. If recalculated for Pt=195.23, K=39.096, value for K/Cl=0.02029. If further corrected for systematic error of method K/Cl=0.02015 (see text).

† 0.02008 if Br is reckoned as Cl as in all the other analyses.

‡ All the samples were pooled together, and only two analyses were made by each method.

§ 0.02036 when corrected for atomic weights of K and Pt. This pair of analyses was performed by a modification of Dittmar's method; another pair analysed by Dittmar's method (but rejected by Makin in favour of the pair already mentioned) gave K/Cl=0.01974, which corrected for atomic weights=0.02006.

|| Quoted by Clarke (1924), but not traceable elsewhere.

¶ Quoted by Thompson & Robinson (1932), but apparently not published elsewhere.

In all cases in which the method is described it consisted in precipitation of the potassium as chloroplatinate, which was either weighed as such or more usually converted to platinum. Of all the authors cited, however, Dittmar alone seems to have made careful trials of his method on synthetic sea water. Some of his deductions from these trials are somewhat vitiated by the erroneous values which he took

for atomic weights, which not only affect the ratio between the weight of platinum in the analyses of natural sea water and the weight of potassium it represents, but also give a different significance to the trial analyses. If these are recalculated for the correct atomic weights it is clear that his method gave slightly high results for all concentrations of potassium, and not, as he thought, only for low concentrations. One is therefore justified in applying a further correction of  $-0.65\%$  to his results, which brings the value of  $K/Cl$  to  $0.02015$ .

Of the remaining authors Makin and Macallum used methods similar to Dittmar's, and their values,  $0.02004$  and  $0.02025$  respectively, agree fairly well with his. It may therefore be concluded that the mean of these three figures ( $K/Cl = 0.02015$ ) is not far from the truth. The analyses described below agree well with this.

### *Experimental*

For the estimation of potassium the method employed was an adaptation to a larger scale of the micro-method described by Robertson & Webb (1939). This had been tested out exhaustively on sea water and found to be fairly satisfactory; and since the greatest source of error appeared to be loss of precipitate in the form of surface film during centrifuging and washing, it was hoped that the error might be considerably reduced if filtration could be substituted for centrifuging. This appears to be the case.

The method consists in precipitating the potassium as potassium silver cobaltinitrite and estimating the precipitate volumetrically by oxidation with ceric sulphate.

10 ml. of sea water were measured into a silica crucible,  $0.3$  ml. of purest concentrated sulphuric acid added, and the whole evaporated on a steam bath and then heated for half an hour in a muffle furnace at  $750^{\circ}\text{C}$ . The salts were extracted with water, and the solution, which was tested and found to be neutral, transferred to a beaker and made up to  $50$  ml. It was then heated to  $75^{\circ}\text{C}$ ., and to it were added  $20$  ml. of a freshly made solution containing  $125$  g. sodium cobaltinitrite and  $5$  g. silver nitrate per litre. Finally  $10$  ml. of pure acetone were added and the beaker left to stand for at least  $12$  hr. at a constant temperature ( $10^{\circ}\text{C}$ .). The precipitate was filtered off through a sintered glass Buchner funnel and well washed with its own saturated solution in distilled water.  $50$  ml. of a solution of ceric sulphate, approximately  $0.02\text{ }N$  in  $N$  sulphuric acid, were measured out and heated up to boiling. This was then run through the filter and collected in a clean receiver. If all the precipitate had not dissolved the liquid was heated up and run through again. The filter was then washed out with distilled water which was added to the filtrate, and the ceric sulphate remaining in the solution was titrated with approximately  $0.02\text{ }N$  ferrous ammonium sulphate solution, made up in  $0.1\text{ }N$  sulphuric acid. Lissamine green was used as indicator.

Standards were run simultaneously, consisting of  $10$  ml. of a solution containing  $0.8468$  g.  $\text{K}_2\text{SO}_4$  ( $=0.3800$  g.  $\text{K}$ ) per litre.

Three separate analyses were performed, each consisting of two samples of the sea water and two standards. The results are shown in Table II.

Table II

No. of analysis	Precipitation time (hr.)		Titration (ml.)	K content (mg.)
I	41	1st standard	21.52	
		2nd standard	21.39	
		Mean	21.45	3.800
		1st sample	21.30	3.818
		2nd sample	21.21	3.829
		50 ml. ceric sulphate solution	52.30	
II	16	1st standard	25.16	
		2nd standard	24.95	
		Mean	25.06	3.800
		1st sample	25.61	3.728
		2nd sample	25.13	3.790
		50 ml. ceric sulphate solution	54.20	
III	20	1st standard	23.68	
		2nd standard	23.75	
		Mean	23.72	3.800
		1st sample	23.80	3.790
		2nd sample	24.07	3.781
		50 ml. ceric sulphate solution	54.20	

The mean of the six figures for the potassium content of 10 ml. of the sea water is 3.789 mg. This corresponds to a K/Cl ratio of 0.02009. It seems reasonable to assume that this does not differ from the true value by more than 1 %.

## SODIUM

The figures for the Na/Cl ratio arrived at by various analysts show far less variation than do those for the K/Cl ratio, and the experimental results detailed below would be scarcely worth putting on record were it not possible to justify them by indirect argument. The figures cited from previous authors by Thompson & Robinson (1932) range from 0.5476 to 0.5567, with a mean of 0.5513. It seems probable however that the true value of the Na/Cl ratio lies closer to the upper limit of this range than to the mean.

### *Experimental*

Four analyses were performed by the micro-method described by Robertson & Webb (1939). No appreciable increase in accuracy would have been gained by taking larger quantities, for, excluding systematic errors inherent in the method, the only errors to which the micro-method is exposed are those of weighing and of a single pipette delivery. The latter does not exceed 0.1 %, and the weighing error is smaller still.

Table III shows the results obtained, using 1 ml. samples.

Table III

Weight of precipitate (mg.)	Weight of sodium (mg.)	Na/Cl
700.2	10.467	0.5550
700.0	10.465	0.5549
699.3	10.454	0.5543
700.7	10.475	0.5554
	Mean	0.5549

*Theoretical*

As already mentioned a similar figure may be arrived at indirectly. It is clear that a balance sheet may be drawn up for sea water in which the sum of the cations must be equivalent to the sum of the anions plus the excess base. Using for the  $\text{SO}_4/\text{Cl}$ ,  $\text{Ca}/\text{Cl}$  and  $\text{Mg}/\text{Cl}$  ratios the figures of Thompson and his co-workers already quoted, for  $\text{K}/\text{Cl}$  the figure suggested in the earlier part of this paper (allowing a possible error of 3 %), and for the excess base figures derived from the data furnished by Wattenberg (1933) for "specific alkalinity", the balance sheet appears as in Table IV.

Table IV

Anions					Cations				
	Parts per 100 of Cl		Equivalents			Parts per 100 of Cl		Equivalents	
	Max.	Min.	Max.	Min.		Max.	Min.	Max.	Min.
Cl*	100	100	2.8203	2.8203	Mg	6.714	6.674	0.5521	0.5488
SO <sub>4</sub>	13.99	13.93	0.2913	0.2900	Ca†	2.133	2.111	0.1064	0.1053
			3.1116	3.1103	K	2.069	1.949	0.0520	0.0498
								0.7114	0.7039
Excess base			0.0123	0.0120	Na	55.44	55.65	2.4109	2.4200
			3.1239	3.1223				3.1223	3.1239

\* Including Br.

† Including Sr.

By this means a value of  $0.5554 \pm 0.001$  is arrived at. It is difficult to see how this figure can be seriously wrong unless some relatively grave analytical error in the determination of one of the other ionic ratios has escaped notice, which seems exceedingly unlikely.

The sodium content may also be deduced, though with less certainty, from a knowledge of the relation between chlorinity and salinity. Since Knudsen's (1901) formula for salinity includes a constant term as well as one dependent on the chlorinity, it is necessary to make the calculation for a particular value of the chlorinity. For a water whose chlorinity is 19 ‰ the solids, other than sodium, known to be present in solution are set out in Table V.

Table V

	g. per kg.
Cl (incl. Br)	19.0000
SO <sub>4</sub>	2.6524
K	0.3819
Ca	0.3969
Sr	0.0119
Mg	1.2719
Excess base as O	0.0185
F, Si, B, etc.	0.0075
	23.7410

In this table it is assumed that Br is replaced by Cl and carbonates converted to oxides, since these are the conditions under which salinity determinations are made. Now the salinity of a water of 19 ‰ chlorinity, i.e. the total weight of solids present, is, according to Knudsen's formula, 34.335 g. per kg. It follows therefore that the sodium content is 34.335-23.741, that is 10.594 g. per kg., and hence that the Na/Cl ratio is 0.5580. This figure is almost certainly too high, and the error is due presumably to the very great difficulties encountered in making accurate determinations of salinity, but it provides confirmatory evidence for supposing that of the values hitherto suggested the higher are more likely to be correct.

## SUMMARY

The sodium and potassium content of sea water have been re-determined. The following values are suggested:  $K/Cl = 0.02009 \pm 0.0002$ ;  $Na/Cl = 0.5549 \pm 0.001$ .

## REFERENCES

- CLARKE, F. W. (1924). *Bull. U.S. Geol. Survey*, no. 770.  
 DITTMAR, W. (1884). *Challenger Reports, Physics and Chemistry*, 1.  
 FORSBERG (1883). *Vega Exped. Rep.* 2, 376.  
 KNUDSEN, M. (1901). *Hydrographische Tabellen*. Copenhagen.  
 KOLOTOFF, S. (1893). *J. Russ. Phys. Chem. Soc.* 24, 82.  
 MACALLUM, A. B. (1903). *J. Physiol.* 29, 213.  
 MAKIN, C. J. S. (1898). *Chem. News*, 77, 171.  
 NATTERER, K. (1892-4). *Mh. Chem.* 13, 873, 897; 14, 624; 15, 530.  
 ROBERTSON, J. D. & WEBB, D. A. (1939). *J. exp. Biol.* 16, 155.  
 SCHLOESING, T. (1906). *C.R. Acad. Sci., Paris*, 142, 320.  
 SCHMELK, L. (1882). *Norske Nordhavs Exped.* 9.  
 THOMPSON, T. G., JOHNSTON, W. R. & WIRTH, H. E. (1931). *J. Cons. int. Explor. Mer*, 6, 246.  
 THOMPSON, T. G. & ROBINSON, R. J. (1932). *Bull. nat. Res. Coun., Wash.*, 85, 95.  
 THOMPSON, T. G. & WRIGHT, C. C. (1930). *J. Amer. chem. Soc.* 52, 915.  
 WATTENBERG, H. (1933). *Wiss. Ergeb. dtsch. Atlant. Exped. "Meteor"*, 8, 157.  
 WHEELER, A. S. (1910). *J. Amer. chem. Soc.* 32, 646.