Chemical Studies of the Western Pacific Ocean. IV.
The Refractive Index of Sea Water.

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The refractive index of sea water was measured for the first time by J. Soret and Ed. Sarasin(1) in 1889. In 1900, H. Tornöe(2) studied the same subject and expressed the relation between salinity and refractive index by the next empirical formula:

$$\log n_{\mathrm{D}}^{17\,5}/S = 6.14340 - 0.00006 \cdot S\,,$$

where n is the refractive index and S, the salinity. Apparently it seems possible to determine the salinity by applying this equation without resorting to the tedious volumetric method; however, it is to be regretted that the accuracy of the results thus obtained is far too inferior.

After Tornöe, attempts by O. Krümmel(3) and other later investigators in improving the new method to the state of practical application for determination of salinity proved fruitless. For instance, M. C. Vauraburg(4) obtained a convenient formula expressing the relation between refractive index and density of sea water at various temperatures, however, the accuracy of the results obtained by this formula barely approaches the order of that of an ordinary aerometer. In 1924, C. Pape(5) finally succeeded in the exact determination of salinity from the refractive index of water by measuring the minute differences between the refractive indices of standard water and samples with an interferometer of high precision. By this method, we can easily determine the salinity very precisely and in a few minutes. The chief object of the present work lies not in the determination of salinity but in a study leading to a stoichiometrical explanation of the refractive index of sea water.

Experimental. The Pulfrich's refractometer made by Fuess was used throughout the experiments. Sea water collected on March 16th, 1938 at N 42°38′, E 145°14′, was divided into ten samples of various chlorinities by dilution with water. The refractive index of each sample was carefully measured with Mazda's sodium lamp at 25°C. The results of the measurements are shown in Table 1.

As shown in Fig. 1, the relation between refractive index and chlorinity is almost linear and may be represented by the next empirical formula:

$$n_{\mathrm{D}}^{25} = 1.33249_7 + 0.000334\,\mathrm{Cl} \qquad (1).$$

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(1) J. Soret and Ed. Sarasin, *Compt. rend.*, **108** (1889), 1248.

(2) H. Tornöe, *Rep. Norw. Fish. Mar. Invest.*, **1** (1900), No. 6.

(3) O. Krümmel, "Handbuch der Ozeanographie", I, Stuttgart (1907).

(4) M. C. Vauraburg, *Compt. rend.*, **172** (1921), 863.

(5) C. Pape, *Ann. d. Hydrog.*, **53** (1924), 249; Schumacher, *Z. Ges. Erdk.* I, **47** (1926), 251.

Table 1. The Relation between Refractive Index and Chlorinity.

n	Cl‰	n	Cl‰
1.33863	18.54	1 33498	7.53
1.33812	16.73	1.33437	5.66
1.33742	14.80	1.33369	3.79
1.33681	13.07	1.33303	1.90
1.33629	11.23	1.33250	0.00
1.33559	9.37		

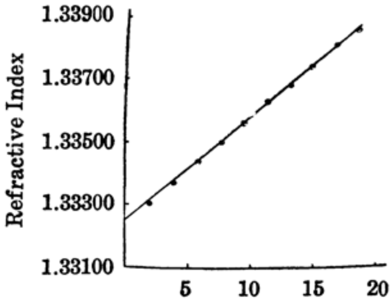

Fig. 1.

For the refractive index of pure water at 25°C., the average of the three values, 1.33251 (Hall and Payne), 1.33248 (Baxter and Burgess) and 1.33250 (measured by the author), was adopted.

The Refractive Index of Artificial Sea Water. It seems to be evident that the difference between the refractive index of pure water and sea water depends mainly upon the salts contained in the latter. It is of interest to know whether the refractive index of an artificial sea water is identical or not with that of a natural sea water of the same degree of chlorinity. An artificial sea water was prepared with chlorinity equivalent to 18.54‰ and its refractive index was measured. As shown in Table 2, the refractive index of the artificial sea water was in good agreement with that of natural sea water.

Table 2. A Comparison between the Refractive Index of Artificial and Natural Sea Waters of the same Chlorinity. Cl‰ 18.54.

Sea Water	Artificial	Natural
n_D^{25}	1.33863	1.33863

In the next place, we may expect that when we dissolve the respective salts individually in water and measure the refractive index ν of each solution, the relation shown in the next formula should hold.

$$n = n_0 + \sum(\nu - n_0) \qquad (2),$$

where n is the refractive index of sea water; ν, the refractive index of each solution; n_0, the refractive index of distilled water.

Table 3 shows the results of the experiment.

Table 3.

Salt	g/l	ν	$\nu - n_0$
$NaCl$	26.4738	1.33707	0.00457
KCl	0.6922	1.33259	0.00009
$MgCl_2$	3.4112	1.33294	0.00044
$MgSO_4$	2.1825	1.33336	0 00086
$CaSO_4$	1.2838	1.33277	0.00027
$CaCO_3$	0.2170	1.33250	0.00000
			$\sum(\nu - n_0) = 0.00623$

$$\boldsymbol{n} = n_0 + \sum(\nu - n_0) = 1.33250 + 0.00623 = 1.33873$$

$$n_{\text{observed}} = 1.33863\ .$$

The results of the measurements described above, prove experimentally that the refraction of sea water is a summation of the individual refractions of pure water and dissolved salts. In the next paragraph, a more theoretical discussion will be given.

A Theoretical Consideration. Inasmuch as sea water is a dilute solution of inorganic salts, the greater part of each salt is dissociated into its ions. So, when refraction of sea water is mentioned, we must usually deal with the ionic refraction instead of molecular refraction. Therefore, since the values of the ionic refraction introduced from the theory of Lorenz-Lorentz have been calculated by Heydweiller⁽⁶⁾ and K. Fajans,⁽⁷⁾ we can easily obtain the equivalent refraction of sea water completely. According to the Lorenz-Lorentz's theory, the equivalent refraction (*E.R.*) of sea water is represented by the next formula:

$$E.R. = \frac{1000\,d}{d}\,\frac{n^2-1}{n^2+2} \qquad (3),$$

where n is the index of refraction of sea water and d, its density. On the other hand, *E.R.* is the sum of the refraction of pure water and of ions of the solute.

Then,

$$E.R. = \frac{1000\,d - S}{d_0}\,\frac{n_0^2-1}{n_0^2+2} + N_{\mathrm{Cl}}R_{\mathrm{Cl}} + N_{\mathrm{Na}}R_{\mathrm{Na}} + N_{\mathrm{SO_4}}R_{\mathrm{SO_4}} + N_{\mathrm{Mg}}R_{\mathrm{Mg}} + N_{\mathrm{Ca}}R_{\mathrm{Ca}} + N_{\mathrm{K}}R_{\mathrm{K}} \qquad (4),$$

where S is the quantity of salt per litre of sea water;
d_0, the density of pure water at 25°C.;
n_0, the refractive index of pure water at 25°C.;
N, the number of mols of each ion;
and R, the refraction of each ion.

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(6) A. Heydweiller, *Ann. Physik*, **41** (1913), 499.

(7) K. Fajans and G. Joos, *Z. Physik*, **23** (1924), 1.

The first term of this formula is the refraction of pure water. Therefore, by knowing every N and R, we may completely evaluate the above formula.

In Table 4, the numerical values of N and R are given.

Table 4.

Ion	N mol/l	R c.c.	$N\times R$ c.c.
Na	0.4542	0.200	0.0908
Cl	0.5352	9.00	4.8168
SO_4	0.0276	14.63	0.4038
Mg	0.0541	−1.57	−0.0850
Ca	0.0108	0.68	0.0731
K	0.0093	2.23	0.0207
		Total	5.3202

The first term is;

$$\frac{1000\,d-S}{d_0}\,\frac{n_0^2-1}{n_0^2+2}=203.533\ \text{c.c.}$$

where,

d, 1.022222 (25°C., Cl‰ 18.54);
d_0, 0.997069 (25°C.);
S, 34.26 g/l;

and

n_0, 1.33249_7 (25°C., Na D-line).

Then, the calculated value of $E.R.$ is;

$$E.R._{\text{calc.}}=208.853\ \text{c.c.}\ .$$

On the other hand the value of $E.R.$ obtained from Formula (3) becomes;

$$E.R._{\text{obs.}}=208.846\ \text{c.c.}\qquad(n=1.33863).$$

The two results are in quite good agreement. Thus we have been able to demonstrate theoretically that the refraction of sea water is a sum of the refractions of pure water and of solute ions.

It is interesting to note that 90% of the ionic refraction is due to the chloride ion. There is a parallelism between molecular refraction and molecular volume; probably in this case, the chloride ion may be the one which occupies the largest space in sea water.

Summary.

(1) Refractive indices of sea water of various chlorinities were measured and the following empirical formula was obtained:

$$n_D^{25}=1.33249_7+0.000334\,\text{Cl}$$

(2) An assumption that the refraction of sea water is a summation of the individual refractions of pure water and dissolved salts, was proved both experimentally and theoretically.

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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