The Spectrophotometric Determination of Micro Amounts of Perchlorate by the Solvent-Extraction Method[1]

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It has been reported by Baas Becking, Haldane, and Izard[2] that perchlorate is an important constituent of sea water. If the perchlorate ion is really present in sea water, it is an interesting phenomenon from the geochemical viewpoint. The determination of perchlorate by reducing it to chloride with subsequent titration has been reported[3-5]. Recently, perchlorate has also been determined by the radiochemical method of isotopic dilution[6]. These methods, however, are not suitable for micro quantities of perchlorate.

Nabar and Ramachandran[7] have studied a method for the estimation of perchlorate which is based on the interaction between a known excess of methylene blue and a soluble perchlorate, with a subsequent precipitation of methylene blue perchlorate, and on the photometric estimation of the residual methylene blue. As methylene blue perchlorate is considerably soluble in water, this procedure is subject to serious errors and is also unsuitable for micro amounts of perchlorate Boltz[8] has briefly described a photometric determination of perchlorate depending on the extraction of the complex formed between methylene blue and perchlorate with chloroform; the present authors have investigated this method in greater detail and have reported their findings in a previous paper[9]. However, this method was greatly affected by the temperature upon extraction, owing to the low extration yield, and it did not have a good reproducibility. Lately, it has been found by the present authors that the methylene blue perchlorate is more extractable with dichloroethane than with chloroform. Consequently, the method using extraction with dichloroethane is more sensitive and less affected by temperature than the chloroform method and has a better reproducibility. This improved spectrophotometric method for the determination of perchlorate will be reported on in this paper, and, at the same time, it will be made clear whether or not perchlorate is really present in various sea waters.

Experimental

Apparatus. — The spectrophotometric measurements were made with a Hitachi spectrophotometer, Model EPU-2, with 10.0 mm. cells, at a spectral band width of 1 mμ.

The shaking was done with a Tokiwa shaker, Model TS.

The separation of the organic layer from the aqueous layer was carried out with a separatory funnel approximately 50 ml. fitted in a short leg.

The organic layer was separated from the separatory funnel into a 15 ml. glass tube with a glass stopper.

Materials. — Guaranteed reagent sulfuric acid, 0.1 N.

1,2-Dichloroethane*, guaranteed reagent.

Anhydrous sodium sulfate, guaranteed reagent.

Methylene Blue Solution.—0.030 g. of guaranteed reagent methylene blue ($C_{16}H_{18}N_3ClS \cdot 3H_2O$) was dissolved in distilled water and diluted to 200 ml. with distilled water to give a 4.0×10^{-4} M solution. The solution was stored in a colored bottle and proved to be stable over a period of several months. Recrystallized[7] methylene blue from 50% aqueous alcohol gave the same results as the methylene blue solution mentioned above.

Standard Perchlorate Solution. — Perchloric acid was neutralized with a potassium hydroxide solution to obtain a white precipitate of potassium perchlorate. This was recrystallized and dried at about 130°C for 2 hr. The stock solution which contains 1 mg. of perchlorate ions per ml. was prepared by dissolving 1.393 g. of the potassium perchlorate in distilled water and then diluting it to 1000 ml. The working standard solutions were prepared by diluting the stock solution properly.

Washing Solution.—This was prepared by mixing 10 ml. of 0.1 N sulfuric acid and 20 ml. of the

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[1] Presented at the Scientific Meeting on Chemistry, Tokyo, Nov., 1961, and at the 11th Annual Meeting of the Japan Society for Analytical Chemistry, Hokkaido, July, 1962.

[2] L. G. M. Baas Becking, A. D. Haldane and D. Izard, *Nature*, **182**, 645 (1958).

[3] G. P. Haight, *Jr.*, *Anal. Chem.*, **25**, 642 (1953).

[4] E. A. Burns and R. F. Muraca, ibid., **32**, 1316 (1960).

[5] N. L. Crump and N. C. Johnson, ibid., **27**, 1007 (1955).

[6] J. K. Johannesson, ibid., **34**, 1111 (1962).

[7] G. M. Nabar and C. R. Ramachandran, ibid., **31**, 263 (1959).

[8] D. F. Boltz, "Colorimetric Determination of Nonmetals", Interscience Publishers, New York (1958), p. 176; W. Holland, H. S. Brand and D. F. Boltz, unpublished research.

[9] I. Iwasaki, S. Utsumi and C. Kang, *Kogyo Yosui* (*Industrial Water*), **37**, 37(1961).

* The dichloroethane already employed once can be used again after purification.

4.0×10^{-4} M methylene blue solution with 200 ml. of distilled water.

Procedure and Calibration Curves.—10.0 ml. of the standard perchlorate solution is placed in a separatory funnel. Then, 0.5 ml. of 0.1 N sulfuric acid, 1.0 ml. of the 4.0×10^{-4} M methylene blue solution and 10.0 ml. of dichloroethane are added. The separatory funnel is shaken for about 30 sec., whereby the complex formed between methylene blue and perchlorate is extracted into the organic layer. When the two layers have clearly separated, the organic layer is transferred to a glass tube with a glass stopper, about 0.5 g. of the anhydrous sodium sulfate is added, and the mixture is shaken vigorously to make it transparent. The absorbance of the clear solution is measured at 655 mμ, using distilled water as a reference.

The calibration curves (I, II, and III) shown in Fig. 1 were obtained by the procedure with standard perchlorate solutions of known concentrations at 15°C, 20°C and 25°C. As can be seen in Fig. 1, the absorbance and the concentration were in a good linear relationship. Though the temperature has a slight effect, this effect is much less than that in the chloroform method[9].

The extracted complex is very stable; even after 24 hr., no measurable change was found when a glass stopper was used to protect against evaporation of the dichloroethane.

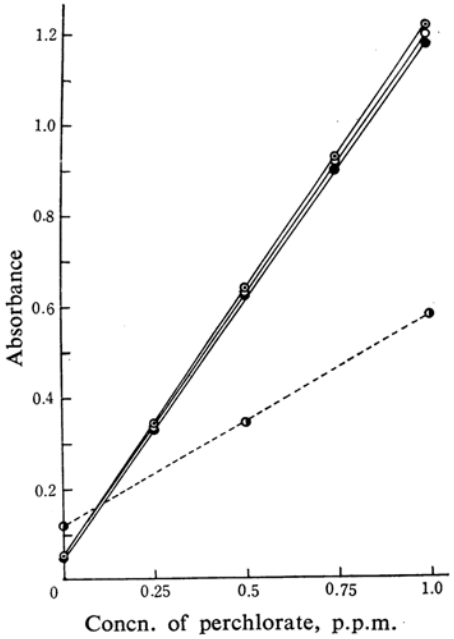

Fig. 1. Calibration curves and effect of temperature.
-⊙- 15°C (I) -○- 20°C (II)
-○- 25°C (III) ---◐--- Chloroform method at 20°C (IV)

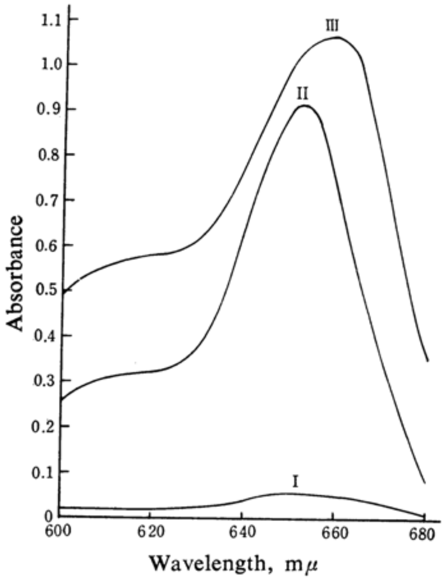

Fig. 2. Spectral absorbance curves.
I Methylene blue in dichloroethane
II Methylene blue perchlorate complex in dichloroethane
III Methylene blue in distilled water

Results and Discussion

Spectral Absorbance Curves.—Figure 2 shows the absorbance curves of an aqueous solution of the methylene blue and dichloroethane solutions of the complex of methylene blue perchlorate and the methylene blue.

The methylene blue perchlorate complex and the reagent blank have a maximum absorbance at 655 mμ (see I and II); on the other hand, the aqueous solution of methylene blue has a maximum at 660 mμ (see III).

The peak at 655 mμ was used in all subsequent measurements because the difference in the absorbance between the complex of methylene blue perchlorate and the reagent blank is greatest at this wavelength.

Extraction by Organic Solvents.—Benzene, carbon tetrachloride, ethyl ether, butyl alcohol, isoamyl alcohol, *n*-hexyl alcohol, tributyl phosphate, chloroform, and 1,2-dichloroethane were tried as solvent for this extraction. Nonpolar solvents such as benzene and carbon tetrachloride proved not to be useful. Only 1,2-dichloroethane and chloroform proved useful. The former, being the better extracting agent, was used in this work. It was found most practical to use a one 10 ml. portion of the solvent in the extraction. Figure 3 shows how the complex of methylene blue and perchlorate is extrated with 10 ml. of dichloroethane.

The extraction yield using one 10 ml. portion of dichloroethane is about 95%. Consequently, the sensitivity of this method is much greater than that of the chloroform method, as can be seen in Fig. 1.

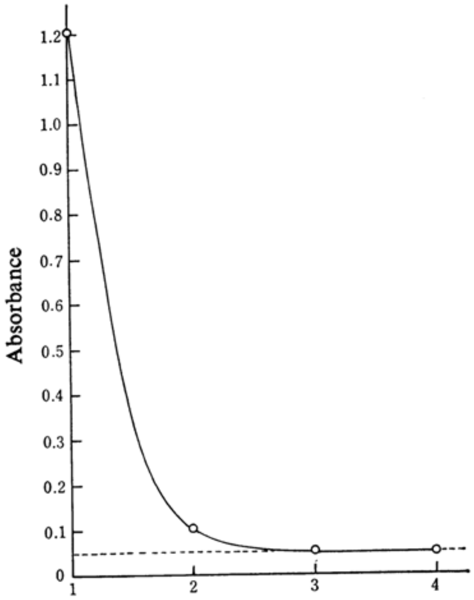

Fig. 3. Experiment for the extraction by dichloroethane.
Concn. of perchlorate: 1 p. p. m.
----: Reagent blank

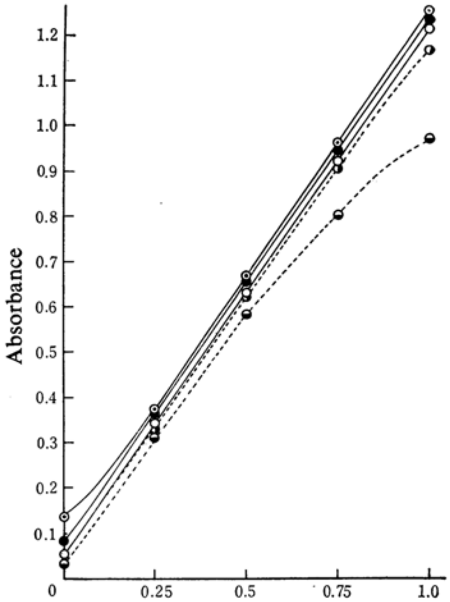

Fig. 4. Effect of concentration of methylene blue. The volume of methylene blue solution added is 1 ml.
---◒--- 1.3×10^{-4} M (I)
---◐--- 2.6×10^{-4} M (II)
—○— 4.0×10^{-4} M (III)
—●— 8.0×10^{-4} M (IV)
—⊙— 1.3×10^{-3} M (V)

The Effect of the Concentration of Methylene Blue Reagent.—The methylene blue perchlorate complex with a 1.3×10^{-4} M methylene blue solution obeyed Beer's law up to about 0.6 p.p.m. of perchlorate, while that with a 2.6×10^{-4} M solution did so up to about 0.8 p.p.m. However, they then showed an increasing deviation from Beer's law for concentrations higher than 0.6 p.p.m. and 0.8 p.p.m. respectively (see I and II in Fig. 4). On the other hand, the higher the concentration of methylene blue was, the higher the absorbance of reagent blank became, and the absorbances, shown in Fig. 4 (see IV and V), did not form a straight line.

Figure 4 shows that the most suitable concentration of the methylene blue solution for the range up to 1 p. p. m. of perchlorate ions is 4.0×10^{-4} M.

The Effect of the Sulfuric Acid Concentration.—When the aqueous solution is alkaline, the dichloroethane extracts become pink, so the procedure should be carried out below a pH value of 6. Sulfuric acid is used for making the aqueous solution acid. The effect of sulfuric acid concentrations on the method is shown in Fig. 5.

The extractability of methylene blue itself increases, while that of the complex does not undergo any measurable change upon an increase in the concentration of sulfuric acid. Therefore, 0.5 ml. of 0.1 N sulfuric acid was added in the present work.

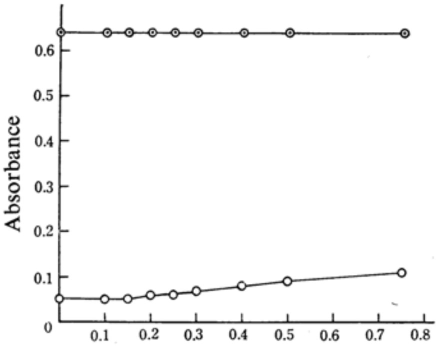

Fig. 5. Effect of sulfuric acid concentration. The volume of sulfuric acid added is 0.5 ml.
—⊙— 0.5 p. p. m. ClO_4^-
—○— Reagent blank

TABLE I. EFFECT OF SHAKING TIME ON EXTRACTION

Time sec.	Absorbance	
	Reagent blank	0.5 p. p. m. ClO_4^-
15	0.060, 0.058	0.635, 0.637
30	0.052, 0.054	0.638, 0.639
60	0.052, 0.051	0.639, 0.639

TABLE II. EFFECT OF DIVERSE IONS

Ion	Added as	Concn. p. p. m.	Absorbance					
					Back washing		Masking with 50 p. p. m. Hg^{2+}	
			Reagent blank	0.5 p. p. m. ClO_4^-	Reagent blank	0.5 p. p. m. ClO_4^-	Reagent blank	0.5 p. p. m. ClO_4^-
None		0	0.054	0.630	0.054	0.629	0.052	0.626
Cl^-	NaCl	10	0.129	0.629			0.099	0.633
		10000	0.977	>1.250	0.057	0.594		
		20000	1.226	>1.250	0.068	0.577		
Br^-	KBr	10	0.306	0.721	0.065	0.635	0.080	0.624
		100	0.774	1.094	0.093	0.629	>1.250	>1.250
I^-	KI	0.1	0.118	0.659	0.101	0.655	0.044	0.621
		1	0.510	0.915	0.368	0.812	0.055	0.624
		10	>1.250	>1.250			0.068	0.630
SCN^-	KSCN	0.5	0.660	1.112	0.498	0.921	0.046	0.629
		1	1.005	>1.250	0.708	1.104	0.051	0.623

TABLE III. EFFECT OF DIVERSE IONS

Ion	Added as	Concn. p. p. m.	Absorbance			
					Back washing	
			Reagent blank	0.5 p. p. m. ClO_4^-	Reagent blank	0.5 p. p. m. ClO_4^-
None	None	0	0.054	0.630	0.054	0.629
IO_4^-	$NaIO_4$	1	0.557	1.138	0.476	1.028
ClO_3^-	$KClO_3$	1	0.261	0.720	0.113	0.646
BrO_3^-	$KBrO_3$	100	0.400	0.786	0.063	0.633
IO_3^-	KIO_3	1000	0.069	0.634		
NO_3^-	KNO_3	10	0.749	1.041	0.166	0.645
NO_2^-	$NaNO_2$	10	0.159	0.655	0.103	0.632
SO_4^{2-}	K_2SO_4	5000	0.073	0.630		
SO_3^{2-}	$Na_2SO_3\cdot 7H_2O$	100	0.135	0.651	0.060	0.631
$S_2O_3^{2-}$	$Na_2S_2O_3\cdot 5H_2O$	10	0.358	0.743	0.100	0.645
S^{2-}	$Na_2S\cdot 9H_2O$	10	0.060	0.631		
MnO_4^-	$KMnO_4$	10	0.079	0.592		
CrO_4^{2-}	K_2CrO_4	10	0.608	0.974	0.156	0.649
MoO_4^{2-}	Na_2MoO_4	10	0.067	0.644		
WO_4^{2-}	$Na_2WO_4\cdot 2H_2O$	10	0.111	0.664	0.096	0.665
VO_3^-	KVO_3	10	0.072	0.647		
$Fe(CN)_6^{3-}$	$K_3Fe(CN)_6$	10	0.062	0.615		
$Fe(CN)_6^{4-}$	$K_4Fe(CN)_6\cdot 3H_2O$	10	0.046	0.621		

The Effect of the Shaking Time on Extraction.—The shaking time on extraction did not change the absorbance. The results listed in Table I show that shaking for 30 sec. is sufficient to extract the complex from the aqueous solution.

The Composition of the Complex between Methylene Blue and Perchlorate.—Application of the continuous variation method[10-13] indicated that only a 1 to 1 complex of methylene blue and perchlorate was formed. The resulting curves, in which the reagent blank was subtracted, are shown in Fig. 6. All the curves have a broad maximum in the vicinity of $x=5$, indicating that the complex is partially dissociated in the aqueous solution and that the extraction yield of the complex by dichloroethane is not 100%.

Effect of Diverse Ions. — In measuring the effect of diverse ions on this method, the experiments were made both in the presence of 0.5 p. p. m. of perchlorate ions and in its absence. The experimental results are given in Tables II, III, IV and V.

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[10] Y. Shibata, T. Inouye, and Y. Nakatsuka, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **42**, 983 (1921).

[11] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

[12] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

[13] R. K. Gould and W. C. Vosburgh, ibid., **64**, 1630 (1942).

TABLE IV. EFFECT OF DIVERSE IONS

Ion	Added as	Concn. p. p. m.	Absorbance	
			Reagent blank	0.5 p. p. m. ClO_4^-
None		0	0.054	0.630
$H_2PO_4^-$	$NaH_2PO_4 \cdot H_2O$	100	0.074	0.639
$HAsO_4^{2-}$	$Na_2HAsO_4 \cdot 7H_2O$	100	0.077	0.635
SeO_4^{2-}	K_2SeO_4	10	0.064	0.627
		100	0.145	0.676
CO_3^{2-}	Na_2CO_3	100	0.072	0.639
CN^-	KCN	10	0.059	0.621
		100	0.126	0.649
F^-	NaF	100	0.079	0.630
Silicate ion	(as SiO_2)	10	0.077	0.639
Borate ion	H_3BO_3	100	0.065	0.625
CH_3COO^-	$CH_3COONa \cdot 3H_2O$	100	0.060	0.645
$C_2O_4^{2-}$	$K_2C_2O_4 \cdot H_2O$	10	0.057	0.621
		100	0.144	0.661

TABLE V. EFFECT OF DIVERSE IONS

Ion	Added as	Concn. p. p. m.	Absorbance			
			Reagent blank	0.5 p. p. m. ClO_4^-	Back washing	
					Reagent blank	0.5 p. p. m. ClO_4^-
None		0	0.054	0.630	0.054	0.629
Na^+	$Na_2SO_4 \cdot 10H_2O$	5000	0.060	0.629		
NH_4^+	$(NH_4)_2SO_4$	5000	0.075	0.626		
Mg^{2+}	$MgSO_4$	1000	0.339	0.762	0.104	0.627
Ca^{2+}	$CaSO_4 \cdot 2H_2O$	280	0.064	0.630		
Sr^{2+}	$SrSO_4$	10	0.267	0.716	0.089	0.631
Al^{3+}	$Al_2(SO_4)_3 \cdot 18H_2O$	100	0.084	0.631		
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	100	0.057	0.631		
Ag^+	Ag_2SO_4	100	0.194	0.673	0.079	0.622
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	100	0.064	0.630		
Cd^{2+}	$3CdSO_4 + 8H_2O$	100	0.146	0.665	0.077	0.629
Hg^{2+}	$HgSO_4$	50	0.052	0.626		
Pb^{2+}	$PbSO_4 \cdot 7H_2O$	10	0.122	0.641	0.075	0.625
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	100	0.059	0.627		
Fe^{3+}	$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	100	0.062	0.624		
Fe^{2+}	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	100	0.078	0.629		
Co^{2+}	$CoSO_4 \cdot 7H_2O$	10	0.063	0.630		
		100	0.103	0.643		
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	10	0.054	0.635		
		100	0.109	0.643		
	H_2O_2	100	0.072	0.628		

There are relatively many anions which cause interference. Sodium, potassium, ammonium, and sulfate do not interfere, however, even when present in amounts of 5000 p. p. m., and the iodate does not interfere at a 1000 p. p. m. It is of interst that halide, when listed in order of increasing interference in this method, are chloride, bromide and iodide, while the oxyacid of the halogens are listed, on the contrary, as iodate, bromate and chlorate. The thiocyanate and iodide, which interfere remarkably even at 0.1 p. p. m., could be masked up to 1 p. p. m. by the addition of 50 p. p. m. of mercuric ion.

The Determination of Perchlorate in the Presence of Other Ions.—Several methods were tried by the present authors to determine the trace amounts of perchlorate in the high concentration of chloride as great as that in sea water. Of these, the back-washing method gave the most satisfactory results for removing chloride and other interfering ions

TABLE VI. EXPERIMENTS FOR THE PERCHLORATE ION IN SEA WATERS

Sea water	Sample taken, ml.	Diluted twice, absorbance	ClO_4^- found, p. p. m.	ClO_4^- added p. p. m.	ClO_4^- recovered p. p. m.
Artificial sea water	5.0	0.079	0	0.10	0.10
Standard sea water	5.0	0.081	no detected	0.10	0.10
Old sea water* No. 1	5.0	0.072	no detected	0.10	0.10
Fresh sea water** No. 2	5.0	0.072	no detected	0.10	0.10
Fresh sea water** No. 3	5.0	0.074	no detected	0.10	0.09

* Determined after three months since the sample was taken 10 km. apart from the north coast of O-sima, Tokyo, March, 1962.

** Samples from two stations on the coast of the Boso Peninsula, Chiba Prefecture, June, 1962.

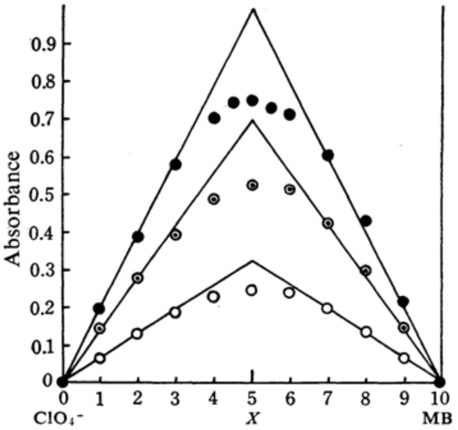

Fig. 6. Method of continuous variation. Concentrations of methylene blue, and perchlorate: 2×10^{-5} M

○ 610 mμ ⊙ 665 mμ ● 655 mμ

to such amounts as are present in sea water.

In order to remove the interfering ions, transfer the organic layer which was separated from the aqueous solution by the procedure mentioned above into another separatory funnel, add 10.0 ml. of the washing solution, and shake for about 30 sec. After the two layers have clearly separated, transfer the organic layer to a glass tube, make it transparent with anhydrous sodium sulfate, and measure the absorbance at 655 mμ.

The results listed in Table II show that one washing is sufficient to eliminate the interference of a 10000 p. p. m. concentration of chloride ions. On the other hand, thiocyanate, periodate, iodide, chlorate, nitrate and nitrite which give remarkably higher results even in small amounts, could not be removed even after two washings. However, most of them are not present in sea water, and the concentration of iodide is too small to consider its interference.

Figure 7 shows the calibration curves of perchlorate ions in the presence of a 10000 p. p. m.

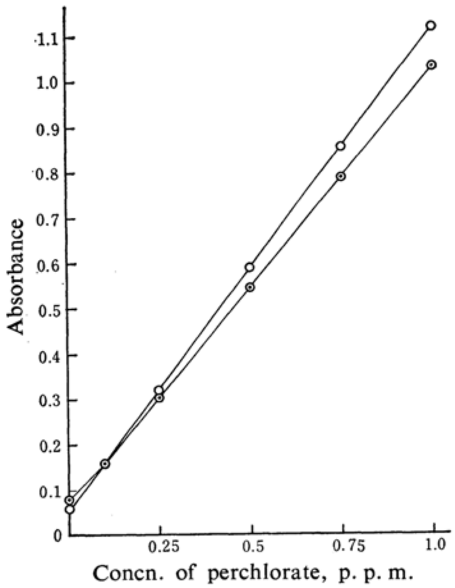

Fig. 7. Calibration curves in the presence of other ions.

-⊙- In artificial sea water diluted twice (I)

-○- In the presence of 10000 p. p. m. Cl^- (II)

of chloride (II) and in artificial sea water[14] diluted twice (I).

The difference between I and II is due in all probability to the fact that there are interfering ions besides chloride in sea water.

The calibration curve (I) was in a good linear relationship for the range from 0.1 to 1.0 p. p. m. of perchlorate ions, but it was not for concentrations lower than 0.1 p. p. m., probably owing to the incomplete removal of magnesium, bromide, and iodide. The concentration of perchlorate in sea water can be readily determined by reference to curve I in

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[14] J. Lyman and R. H. Fleming, *J. Marine Research*, 3, 134 (1940).

Fig. 7. It was reproducible within the error of ±0.02 p. p. m. of perchlorate ions. It is possible to determine the perchlorate over the range from 0.05 p. p. m. to 2.0 p. p. m. in sea water by this method.

Experiment for the Perchlorate in Various Sea Waters.—Some results of the application of this method to several sea waters are given in Table VI.

As will be seen in Table VI, the experimental results show that the concentration of perchlorate in sea water, if present, is below 0.05 p. p. m., very much less than the figures reported by Baas Becking, Haldane and Izard(2).

Greenhaigh and Riley(15) have investigated the occurrence of perchlorate in sea water by a method they themselves devised, and Johannesson(6) has applied the radiochemical method of isotopic dilution to its determination in sea water. They also detected no perchlorate in natural sea water within the sensitivities of their methods.

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15) R. Greenhaigh and J. P. Riley, *Nature*, **187**, 1107 (1960).