The Colorimetric Determination of Minute Amounts of Iodide and Iodate in Sea Water by Means of Their Catalytic Effects

By Norinobu YONEHARA

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It is known that iodine in sea water exists in the form of both iodide and iodate. Sugawara and Terada(1) determined the iodide and total iodine contents in sea water, but the method they proposed requires a considerable amount of sample and a time-consuming procedure. Barkley and Thompson(2) determined the iodate and total iodine contents in a relatively small amount of sample by using an amperometric or spectrophotometric method. The amperometric method was, however, accompanied by a somewhat complicated procedure, while the spectrophotometric method was applicable only to the determination of total iodine. The present author and others have reported in a preceding paper(3) a colorimetric method for the determination of ultramicro amounts of iodine in the form of both iodide and iodate by utilizing their catalytic effect on the color-fading of ferric thoicyanate. By this method, the iodate and total iodine contents in river and rain waters can be determined. However, as for sea water, this method is suitable for determining only the total iodine, but not the iodate iodine, because the separation of iodide from iodate is not performed quantitatively in the presence of the large amount of chloride contained in sea water. In the present work, therefore, the quantitative separation of iodide from iodate in sea water is attempted by means of the oxidation of iodide with an appropriate oxidizing agent. Because it improves the concentration of the reagents concerned and the conditions of the reaction, this catalytic method appears to be more sensitive and accurate than the method previously proposed, at least sensitive and accurate enough to determine the iodate and total iodine contents in sea water.

Experimental

Apparatus.—A Hirama photoelectric-colorimeter with a 460 filter (with maximum transmission at 460 mμ) and 10 mm. cells was used to measure the absorbance.

The reaction was carried out at 60.00±0.05°C using a water bath with a Taiyo Thermo Unit.

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1) K. Sugawara and K. Terada, *J. Earth Sci., Nagoya Univ.*, 5, 81 (1957).

2) R. A. Barkley and J. G. Thompson, *Anal. Chem.*, 32, 154 (1960).

3) I. Iwasaki, S. Utsumi and N. Yonehara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 85, 36 (1964).

Reagents. — All the chemicals used were of guaranteed reagent quality.

Ferric Ammonium Sulfate - Nitric Acid Solution.— Six grams of ferric ammonium sulfate dissolved in 100 ml. of a 7.0 N nitric acid solution was stored in a brown glass bottle.

Potassium Thiocyanate Solution (0.01 M).—A potassium thiocyanate solution (0.1 M), standardized by Volhard's method, was diluted to a 0.01 M solution and stored in a brown glass bottle.

Sodium Nitrite Solution (0.014 M). — Sodium nitrite, 0.483 g. dissolved in redistilled water, was diluted to 500 ml. in a volumetric flask, and stored in a brown glass bottle.

Sodium Chloride Solution (20 g. of Chloride per l.). —Sodium chloride (32.970 g.) was dissolved in redistilled water and diluted to exactly 1 l.

Standard Iodide Solution. — A potassium iodide solution (0.1 M) was standardized by Volhard's method;[4] the working solution was then prepared by diluting this solution adequately.

Standard Iodate Solution. — Potassium iodate 0.843 g. was dissolved in redistilled water and diluted to exactly 500 ml. The working solution was prepared by successive dilutions.

Procedures and Calibration Curves. — The chlorinity of sea water was determined, and then it was diluted with redistilled water, to give a chlorinity of 2%.

Procedure (1) (for the Determination of Total Iodine).—Ten milliliters of the diluted sample is taken into a glass tube. One milliliter of a 0.014 M sodium nitrite solution and 1.0 ml. of a 0.01 M potassium thiocyanate solution are added and thoroughly mixed. The glass tube is then placed in the water bath at 60.0±0.1°C for about 10 min. The reaction is initiated by adding 2.0 ml. of a nitric acid solution of ferric ammonium sulfate (at the same temperature), mixing them thoroughly, and replacing the glass tube in the water bath.

After 20 min. ±5 sec. after the addition of the ferric ammonium sulfate solution, the absorbance of the solution is measured at the wavelength of 460 mμ, using redistilled water as a reference. It is recommended that the solution in the glass tube be removed from the water bath and poured into the cell 20 sec. before the scheduled time.

The calibration curve I shown in Fig. 1 was obtained by procedure 1 by using standard iodide and iodate solutions of known concentrations and containing chloride of the concentration of 2000 p. p. m. As can be seen in Fig. 1, in the cases of iodide and iodate, the absorbance is identical for the corresponding concentrations.

Procedure (2) (for the Determination of Iodate in the Presence of Iodide).—To 10.0 ml. of the diluted sample taken in a separatory funnel, 1.0 ml. of a 0.014 M sodium nitrite solution is added and thoroughly mixed, followed by the addition of 2.0 ml. of a nitric acid solution of ferric ammonium sulfate, mixing, and the further addition of 5 ml. of carbon tetrachloride. The separatory funnel is shaken for about 10 sec. and the layers allowed to separate. The aqueous layer is then transferred to the glass tube; a small amount of carbon tetrachoride does not disturb the subsequent procedure. The glass tube containing the aqueous layer thus obtained is placed in the water bath at 60.0±0.1°C for about 10 min. Then the reaction is initiated by adding 1.0 ml. of a 0.01 M potassium thiocyanate solution (at the same temperature); the solution is mixed thoroughly, and the glass tube with the solution is replaced in the water bath. At 20.0 min. after mixing, the absorbance of the solution is measured in the same way as in procedure 1.

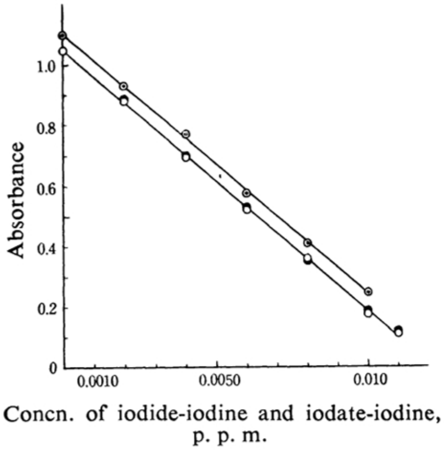

Fig. 1. Calibration curves.
In the presence of 2000 p. p. m. chloride
-○- I^- and -●- IO_3^- (I)
-⊙- IO_3^- (II)

The calibration curve II shown in Fig. 1 was obtained by procedure 2 by using standard iodate solutions of known concentrations and containing chloride of the concentration of 2000 p. p. m.

A difference between calibration curves I and II in Fig. 1 is probably caused by a loss (about 0.2 ml.) of solution during the extraction of procedure 2.

The catalytic reaction should be carried out in a dark place, thus avoiding an acceleration of the fading by sun light.[5]

Results and Discussion

The Effect of the Reaction Time.—Ten milliliters of a 0.010 p. p. m. iodide solution in the presence of 2000 p. p. m. chloride, 1.0 ml. of a 0.014 M sodium nitrite solution, 1.0 ml. of a 0.01 M potassium thiocyanate solution, and 2.0 ml. of a nitric acid solution of ferric ammonium sulfate were mixed and kept at 60°C. Reaction rate curve I shown in Fig. 2 was obtained by measuring the absorbances of this solution at various reaction times. Curves II and III in Fig. 2 were obtained by using a 0.005 p. p. m. iodide solution and redistilled water. It may be seen in Fig. 2 that the reaction rate increases with the amount of iodide and that differences in absorbances

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[4] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley & Sons, Inc., New York (1935), p. 657.

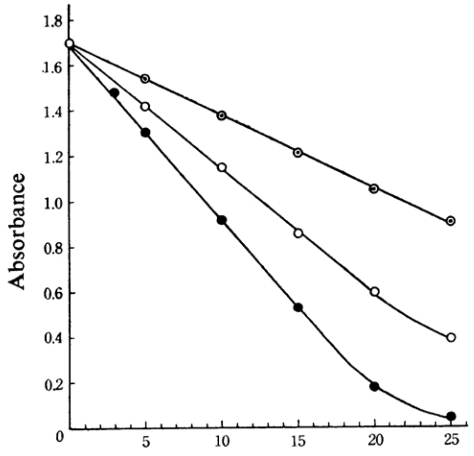

Fig. 2. Reaction rate curves.
60°C, in the presence of 2000 p. p. m. chloride
-●- 0.010 p. p. m. I^- (I)
-○- 0.005 p. p. m. I^- (II)
-⊙- Redistilled water (III)

among the three curves increase with the reaction time. These results indicate that the sensitivity of the method increases with the reaction time. The solution with 0.010 p. p. m. iodide becomes almost colorless after 25 min. A reaction time of 20 min. is adequate because of the high sensitivity.

The Effect of Chloride.—In the absence of chloride, iodate showed a different catalytic effect on the reaction rate than did iodide.5) However, it has been reported by Dubravčić6) that iodate showed the same catalytic effect as iodide in the presence of a large amount of chloride in the ceric-arsenous acid method. The same effect was also found in this color-fading method. In the present work, the effects of chloride have also been examined, therefore.

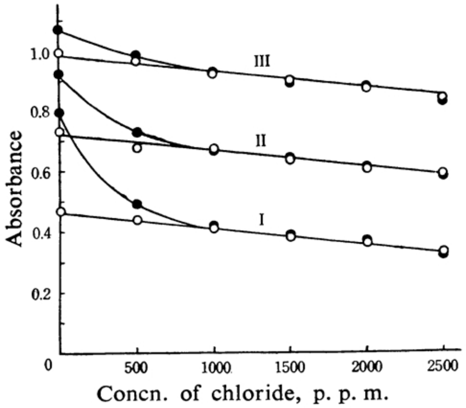

Fig. 3. Effect of concentrations of chloride.
60°C, 20 min.
-○- I^-, -●- IO_3^-
(I) 0.008 p. p. m. iodine
(II) 0.005 p. p. m. iodine
(III) 0.002 p. p. m. iodine

Table I. Check of determination of total iodine in the mixture
(in the presence of 2000 p. p. m. chloride)

Concn. of I^- p. p. m.	Concn. of IO_3^- (as iodine) p. p. m.	Concn. of total iodine p. p. m.	Absorbance	
0.0020	0	0.0020	0.87_9	0.87_9
0.0010	0.0010		0.87_7	0.85_9
0	0.0020		0.87_9	0.88_0
0.0060	0	0.0060	0.53_5	0.53_3
0.0050	0.0010		0.53_9	0.53_9
0.0030	0.0030		0.54_9	0.54_0
0.0020	0.0040		0.52_0	0.52_8
0	0.0060		0.53_8	0.52_6
0.0080	0	0.0080	0.37_3	0.35_5
0.0060	0.0020		0.35_4	0.37_0
0.0040	0.0040		0.35_8	0.37_5
0.0010	0.0070		0.36_5	0.35_3
0	0.0080		0.35_4	0.36_4

Three curves, I, II and III, shown in Fig. 3 were obtained by procedure 1 by using both iodide and iodate solutions containing various amounts of chloride. In the presence of more than 1000 p. p. m. chloride, iodide solutions show the same absorbance as that of iodate solutions in the same concentrations. The presence of 2000 p. p. m. chloride is adequate to determine the amount of total iodine. Sea water diluted ten times, containing chloride of about 2000 p. p. m., is, consequently, suitable for determination by this method. Satisfactory results obtained by using mixtures of iodides and iodates of different concentration ratios are listed in Table I.

The Concentration of Reagents. — A suitable concentration of a sodium nitrite solution was first sought. As iodide and iodate react with each other in an acidic solution, iodide must be oxidized to free iodine and then removed before the iodide-iodate reaction takes place. In the previous paper3) a nitric acid solution of ferric ammonium sulfate was used for oxidation, but in the presence of a large amount of chloride, the separation of iodide from iodate was not quantitative. Both a sodium nitrite solution and a nitric acid solution of ferric ammonium sulfate are used for the oxidation of iodide. These reagents are not only the oxidizing agents, but also the reagents in the catalytic fading reaction. As an

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5) S. Utsumi, M. Shiota, N. Yonehara and I. Iwasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **58**, 32 (1964).

6) M. Dubravčić, *Analyst*, **80**, 149 (1955).

oxidizing agent, 1 ml. of a 0.014 M nitrite solution was necessary for the quantitative separation of iodide from iodate.

After a satisfactory concentration of a nitrite solution was determined, the concentration of the thiocyanate solution was adjusted to provide a suitable calibration curve covering the range from 0.001 to 0.01 p. p. m. of iodine.

The Removal of Iodide. — An attempt was made to remove the iodide of various concentrations in solutions by procedure 2. The results listed in Table II show that satisfactory removals of iodide were carried out by this procedure. Absorbances by using iodide solutions are identical with that of the redistilled water within the range of experimental error.

The results listed in Table III were obtained by precedure 2 in the presence of various amounts of both iodide and iodate. As can be seen in Table III, the iodate remains quantitatively in the aqueous layer, while the iodide is completely removed. In the experiments described above, the extraction in procedure 2 was carried out within 15 min.

TABLE II. REMOVAL OF IODIDE

Concn. of I^- p. p. m.	Absorbance	
Blank	1.09_2	1.08_6
0.002	1.08_6	1.08_1
0.004	1.08_6	1.08_1
0.006	1.08_6	1.07_5
0.008	1.07_1	1.06_6
0.010	1.07_6	1.06_6

TABLE III. REMOVAL OF IODIDE IN THE PRESENCE OF IODATE

Concn. of IO_3^- (as iodine) p. p. m.	Concn. of I^- p. p. m.	Absorbance	
0.0010	0	1.00_9	1.00_0
	0.0020	1.00_4	0.99_1
	0.0050	1.00_0	1.00_0
	0.0090	1.00_4	0.99_1
0.0020	0	0.92_8	0.91_4
	0.0010	0.92_8	0.93_1
	0.0040	0.93_1	0.91_7
	0.0080	0.93_1	0.90_0
0.0040	0	0.76_0	0.77_0
	0.0010	0.76_2	0.78_7
	0.0030	0.77_0	0.76_0
	0.0060	0.78_2	0.79_0
0.0060	0	0.57_2	0.57_5
	0.0020	0.57_7	0.58_2
	0.0040	0.58_5	0.56_9
0.0080	0	0.40_9	0.40_0
	0.0010	0.40_0	0.38_6
	0.0020	0.41_1	0.38_8

TABLE IV. EFFECT OF DIVERSE IONS

Ion	Added as	Concn. p. p. m.	Absorbance Reagent blank	 0.005 p. p. m. I^-	 0.005 p. p. m. IO_3^- (as iodine)
None		0	1.05_1	0.62_0	0.62_5
K^+	KNO_3	100	1.04_6	0.62_0	0.63_8
Mg^{2+}	$Mg(NO_3)_2\cdot6H_2O$	200	1.04_6	0.61_6	0.63_3
Ca^{2+}	$Ca(NO_3)_2\cdot4H_2O$	100	1.04_6	0.60_2	0.62_2
Sr^{2+}	$SrSO_4$	10	1.01_7	0.60_4	0.62_0
Br^-	KBr	50	1.04_6	0.61_4	0.62_2
SO_4^{2-}	K_2SO_4	300	1.04_6	0.58_8	0.60_0
HCO_3^-	$NaHCO_3$	100	1.05_6	0.64_6	0.65_4
Borate ion	H_3BO_3	10	$1\cdot04_6$	0.61_7	0.62_2
Silicate ion	(as SiO_2)	100	1.03_7	0.61_2	0.62_0
F^-	NaF	10	1.04_2	0.61_4	0.62_2
NO_3^-	$NaNO_3$	6200	1.00_9	0.55_1	0.56_5
		1000	1.04_6	0.62_0	0.62_5
PO_4^{3-}	$NaH_2PO_4\cdot H_2O$	100	1.04_6	0.58_8	0.61_4
BrO_3^-	$KBrO_3$	1	1.04_1	0.59_9	0.62_0
CrO_4^{2-}	K_2CrO_4	10	1.00_0	0.58_3	0.58_3
$S_2O_3^{2-}$	$Na_2S_2O_3\cdot5H_2O$	10	0.99_5	0.58_8	0.60_0
ClO_3^-	$KClO_3$	1	1.04_1	0.61_6	0.63_6
Hg^{2+}	$HgSO_4$	0.1	1.05_1	0.78_5	0.79_8
		0.01	1.04_6	0.62_9	0.65_0
Ag^+	Ag_2SO_4	1	1.04_6	0.70_3	0.71_9
		0.1	1.05_0	0.62_0	0.62_0

TABLE V. DETERMINATIONS OF PREPARED MIXTURE SOLUTIONS

Added			Found					
Total iodine p. p. m.	IO_3^- (as iodine) p. p. m.	I^- p. p. m.	Concn. of total iodine p. p. m.		Concn. of IO_3^- (as iodine) p. p. m.		Concn. of I^- p. p. m.	
				error		error		error
0.0020	0.0010	0.0010	0.002_2	+0.0002	0.001_1	+0.0001	0.001_1	+0.0001
			0.002_2	+0.0002	0.001_0	0	0.001_2	+0.0002
	0	0.0020	0.002_2	+0.0002	0.000_1	+0.0001	0.002_1	+0.0001
			0.001_9	−0.0001	0.000_0	0	0.001_9	−0.0001
0.0040	0.0010	0.0030	0.004_2	+0.0002	0.001_1	+0.0001	0.003_1	+0.0001
			0.004_1	+0.0001	0.001_0	0	0.003_1	+0.0001
	0.0020	0.0020	0.004_0	0	0.001_9	−0.0001	0.002_1	+0.0001
			0.004_3	+0.0003	0.002_0	0	0.002_3	+0.0003
	0.0040	0	0.004_0	0	0.003_9	−0.0001	0.000_1	+0.0001
			0.004_0	0	0.003_7	−0.0003	0.000_3	+0.0003
0.0060	0.0010	0.0050	0.006_0	0	0.001_0	0	0.005_0	0
			0.006_2	+0.0002	0.001_1	+0.0001	0.005_1	+0.0001
	0.0030	0.0030	0.005_9	−0.0001	0.002_7	−0.0003	0.003_2	+0.0002
			0.006_0	0	0.002_7	−0.0003	0.003_3	+0.0003
	0.0050	0.0010	0.006_0	0	0.004_9	−0.0001	0.001_1	+0.0001
			0.006_1	+0.0001	0.004_8	−0.0002	0.001_3	+0.0003
	0	0.0060	0.006_0	0	0.000_2	+0.0002	0.005_8	−0.0002
			0.006_1	+0.0001	0.000_1	+0.0001	0.006_0	0
0.0090	0.0010	0.0080	0.008_9	−0.0001	0.001_1	+0.0001	0.007_8	−0.0002
			0.008_9	−0.0001	0.001_1	+0.0001	0.007_8	−0.0002
	0.0020	0.0070	0.008_9	−0.0001	0.001_9	−0.0001	0.007_0	0
			0.009_0	0	0.001_9	−0.0001	0.007_1	+0.0001
	0.0040	0.0050	0.008_9	−0.0001	0.004_0	0	0.004_9	−0.0001
			0.008_9	−0.0001	0.003_7	−0.0003	0.005_2	+0.0002
	0.0060	0.0030	0.009_0	0	0.006_1	+0.0001	0.002_9	−0.0001
			0.008_9	−0.0001	0.005_7	−0.0003	0.003_2	+0.0002
	0.0080	0.0010	0.008_9	−0.0001	0.007_8	−0.0002	0.001_1	+0.0001
			0.009_0	0	0.007_8	−0.0002	0.001_2	+0.0002
	0.0090	0	0.008_8	−0.0002	0.008_8	−0.0002	0.000_0	0
			0.008_9	−0.0001	0.008_9	−0.0001	0.000_0	0

after the addition of the oxidizing agent. However, when this period was prolonged over 40 min., the results did not have a tolerable reproducibility.

The Effect of Diverse Ions.—To make clear the effect of diverse ions on this method, some experiments were made in the presence of 0.005 p. p. m. of both iodide and iodate ions, and in their absence. The experimental results are given in Table IV. Nitrate does not interfere at 1000 p. p. m., but it gives a slightly low absorbance at 6200 p. p. m. (about 0.1 M). Sulfate does not significantly interfere at 300 p. p. m. Oxidizing or reducing agents interfere at relatively low concentrations. Mercury and silver interfere remarkably. Most sea waters do not contain these substances in concentrations which cause serious interference. Most ions commonly occuring in sea water do not interfere.

The Results of Determination.—The determinations of the total iodine and iodate-iodine were made by using mixed solutions containing known amounts of iodide and iodate and 2000 p. p. m. of chloride. The results listed in Table V indicate the maximum error of ±0.0003 μg. per l. Iodide-iodine is calculated by the difference between the total-iodine and the iodate-iodine.

The total iodine and iodate-iodine contents in several sea waters were determined by using sea water diluted about ten and twenty times with the addition of known amounts of chloride to give the concentration of 2000 p. p. m. of chloride. The results listed in Table VI are calculated to original concentrations, and the comparison of the two results mentioned above shows good agreement. The method was also checked by adding known amounts of both iodide and iodate to sea water to show the good recovery of both iodide and iodate (Table VII).

According to these results, it may be concluded that the present method is quite satisfactory for the determination of iodide and iodate contents in sea water.

TABLE VI. DETERMINATIONS OF IODIDE AND IODATE CONTENTS IN SEA WATERS

Sea water		Concn. of total iodine p. p. m.	Concn. of IO_3^- (as iodine) p. p. m.	Concn. of I^- p. p. m.	Chlorinity ‰
Artificial sea water*[1]	Diluted ten times	0.07_1 0.07_0	0.02_1 0.02_0		18.68
	Average	0.07_1	0.02_1	0.05_0	
Standard sea water	Diluted ten times	0.05_6 0.05_5	0.03_5 0.03_4		19.37
	Average	0.05_6	0.03_5	0.02_1	
Sea water*[2] No. 1	Diluted ten times	0.05_2 0.05_4	0.03_4 0.03_4		18.80
	Diluted twenty times	0.05_4 0.05_5	0.03_4 0.03_6		
	Average	0.05_4	0.03_5	0.01_9	
Sea water*[3] No. 2	Diluted ten times	0.05_3 0.05_1	0.04_5 0.04_2		19.37
	Diluted twenty times	0.05_2 0.05_2	0.04_4 0.04_4		
	Average	0.05_2	0.04_4	0.00_8	
Sea water*[4] No. 3	Diluted ten times	0.03_4 0.03_3	0.01_6 0.01_5		18.61
	Diluted twenty times	0.03_6 0.03_4	0.01_6 0.01_4		
	Average	0.03_4	0.01_5	0.01_9	

*[1] Artificial sea water(7) contains 0.050 p. p. m. iodide-iodine and 0.020 p. p. m. iodate-iodine.

*[2] The sample was taken 200 m. apart from the east coast of Satsuma-Iwo-jima, Kagoshima, August, 1962.

*[3] The sample was taken 10 km. apart from the north coast of O-sima, Tokyo, March, 1962.

*[4] The sample was taken on the coast of Mito, Ibaraki, August, 1962.

TABLE VII. DETERMINATIONS OF IODIDE AND IODATE CONTENTS IN SEA WATERS CONTAINING KNOWN ADDED IODIDE AND IODATE

Sample		Concn. of total iodine p. p. m.	Concn. of IO_3^- (as iodine) p. p. m.	Concn. of I^- p. p. m.
No. 1	Originally present	0.05_4	0.03_5	0.01_9
	Added	0.030	0.015	0.015
	Total	0.08_4	0.05_0	0.03_4
	Found*	0.08_4	0.05_1	0.03_3
	Recovered	0.03_0	0.01_6	0.01_4
No. 2	Originally present	0.05_2	0.04_4	0.00_8
	Added	0.030	0.015	0.015
	Total	0.08_2	0.05_9	0.02_3
	Found*	0.08_2	0.05_8	0.02_4
	Recovered	0.03_0	0.01_4	0.01_6
No. 3	Originally present	0.03_4	0.01_5	0.01_9
	Added	0.030	0.015	0.015
	Total	0.06_4	0.03_0	0.03_4
	Found*	0.06_2	0.02_9	0.03_3
	Recovered	0.02_8	0.01_4	0.01_4

* Average of two determinations.

Summary

In the presence of 2000 p. p. m. chloride, iodide and iodate show the same catalytic effect on the color-fading reaction of a solution of ferric thiocyanate. The total iodine content in sea water may be determined by estimating the absorbance of a sample diluted about ten times.

The iodide in the sample is first oxidized to free iodine by a sodium nitrite solution and a nitric acid solution of ferric ammonium sulfate. The resulting free iodine is removed by extraction with carbon tetrachloride. The iodate which remains quantitatively in the aqueous layer is determined by a similar procedure. The difference between the total iodine and the iodate-iodine gives the iodide-iodine.

By this method, the iodate and total iodine contents in sea water can be determined rapidly and accurately. It takes only about 2 ml. of sea water to determine both the total iodine and the iodate-iodine.

The author wishes to express his thanks to Professor Iwaji Iwasaki of the Tokyo Institute of Technology for advice and encouragement given in the course of the work. Thanks

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

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Laboratory of Analytical Chemistry
and Geochemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo