A New Colorimetric Method for the Determination of Minute Amounts of Bromide by Means of Its Catalytic Effect*

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A rapid and sensitive method for the determination of a minute amount of bromide is desirable. Two of the present authors (S. U. and I. I.) and Shiota[1] have previously reported a colorimetric method for the determination of bromide which is based on the catalytic effect of bromide on the oxidation of iodine to iodate by potassium permanganate in a sulfuric acid solution. Fishman and Skougstad[2] have studied this method further. However, it has been observed that some inevitable technical difficulties occur in keeping the reaction time and temperature constant, because this oxidation reaction proceeds fairly rapidly, even below room temperature.

By a further investigation of the oxidation of iodine to iodate employing various oxidizing agents, it was found that, when ceric ammonium sulfate is used as the oxidizing agent, this oxidation reaction is catalytically promoted by a minute amount of bromide in the presence of large amounts of potassium dichromate in a nitric acid solution. This reaction proceeds fairly slowly at room temperature, thus, favorable conditions for the procedure can be realized. In this paper a new method for the determination of a minute amount of bromide using this reaction will be described.

This oxidation reaction proceeds more rapidly in the presence of bromide than in its absence. Consequently, when this reaction was carried out at a given temperature for a given time, the higher the concentration of bromide was, the lower that of the unreacted iodine became. Thus, the determination of bromide can be made by determining the amount of this unreacted iodine. The oxidation reaction is stopped after a given time by the extraction of the unreacted iodine with carbon tetrachloride; the amount of iodine in the extract is then determined by adding an alcoholic solution of mercuric thiocyanate and a ferric ammonium sulfate solution and by measuring the absorbance of the resulting ferric thiocyanate.[3]

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 reactions were carried out at given temperatures (±0.1°C) using a water bath with a Taiyo Thermo Unit.

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

The Ceric Ammonium Sulfate Solution (0.2 M *in 2* N *Sulfuric Acid).*—Dissolve 33.42 g. of ceric ammonium sulfate [$Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 4H_2O$] in a sulfuric acid solution (14 ml. of concentrated sulfuric acid +115 ml. of redistilled water) and dilute to 250 ml. with redistilled water.

The Potassium Dichromate Solution (0.2 M*).*—Dissolve 15.21 g. of potassium dichromate in redistilled water and dilute to 250 ml.

The Potassium Iodide Solution (1 mg. of iodide per ml.).—Recrystallized potassium iodide was used. Prepare about a 0.1 M potassium iodide solution, standardize by Volhard's method, and then dilute this solution to give 1000 p. p. m. of iodide.

Concentrated Nitric Acid (sp. gr. 1.38).

The Mercuric Thiocyanate Solution.—Solid mercuric thiocyanate[4] was prepared in our laboratory. Dissolve 0.3 g. of mercuric thiocyanate in 100 ml. of absolute ethyl alcohol.

The Ferric Ammonium Sulfate Solution.—Dissolve 6 g. of ferric ammonium sulfate in 100 ml. of a 6 N nitric acid solution and store in a brown glass bottle.

The Standard Bromide Solution.—Prepare about a 0.1 M potassium bromide solution using redistilled water and standardize by Volhard's method. Prepare the working solutions by diluting this solution adequately.

The Standard Chloride Solution.—Dissolve 1.649 g. of sodium chloride in redistilled water and dilute to exactly 1 l. This solution contains 1 mg. of chloride per milliliter. Prepare the working solutions by successive dilutions.

Procedure and Calibration Curve. — To 10.0 ml. of the sample in a 30 ml. glass tube with a glass

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[1] M. Shiota, S. Utsumi and I. Iwasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 753 (1959).

[2] M. J. Fishman and M. W. Skougstad, *Anal. Chem.*, **35**, 146 (1963).

[3] S. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 32 (1953); I. Iwasaki, S. Utsumi, A. Tomonari and I. Morita, ibid., **80**, 749 (1959).

[4] S. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 835 (1952); I. Iwasaki, S. Utsumi, K. Hagino and T. Ozawa, This Bulletin, **29**, 860 (1956).

stopper add 1.5 ml. of the potassium iodide solution, 1.0 ml. of the potassium dichromate solution and 2.0 ml. of the nitric acid solution, and mix thoroughly. Place the glass tube in the water bath at 30°C for about 10 min. Start the reaction by adding 2.0 ml. of the ceric ammonium sulfate solution (at the same temperature), mixing thoroughly, and replacing the glass tube in the water bath.

Exactly 20 min. after the addition of the ceric ammonium sulfate solution, add 5 ml. of carbon tetrachloride and immediately shake the glass tube for 30 sec. After the layers have completely separated, remove the aqueous layer by using the pipet with a rubber bulb. As even a small amount of the remaining aqueous layer disturbs the subsequent procedure, it is necessary to remove it completely by the following procedure. Add about 5 ml. of redistilled water to the glass tube containing carbon tetrachloride along the inside wall of the tube, and then remove this water again in the manner described above. The aqueous layer that initially remains can be removed almost completely by repeating this procedure three times. To the carbon tetrachloride thus obtained in the glass tube, add 5.0 ml. of redistilled water, 1.0 ml. of the ferric ammonium sulfate solution and 0.5 ml. of the mercuric thiocyanate solution, and shake the glass tube for about one minute. Thus, the aqueous layer is colored with ferric thiocyanate. Measure the absorbance of this aqueous layer at 460 mμ using redistilled water as a reference.

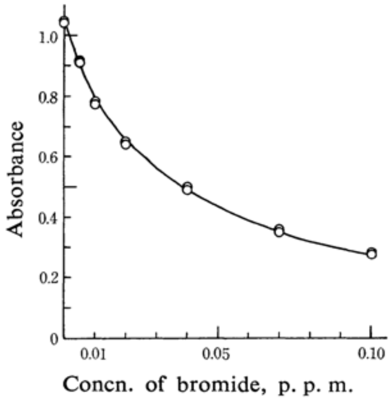

Fig. 1. Calibration curve.
30°C, 20 min.

The calibration curve shown in Fig. 1 was obtained by the procedure described above, using standard bromide solutions of known concentrations. The same calibration curve as that for bromide is obtained by using standard bromate solutions with the concentrations given as bromine.

This method is especially suitable for the determination of concentrations lower than 0.05 p. p. m.; concentrations of bromide as low as 0.005 p. p. m. can thus be determined.

Results and Discussion

The Reaction Rate Curves. — The catalytic reactions were carried out in the same way using 10.0 ml. of a 0.10 p. p. m. bromide solution. After various intervals, the color was developed by using 10.0 ml. of redistilled water, 2.0 ml. of the ferric ammonium sulfate solution and 1.0 ml. of the mercuric thiocyanate solution. The reaction rate curve I shown in Fig. 2 was obtained by this experiment.

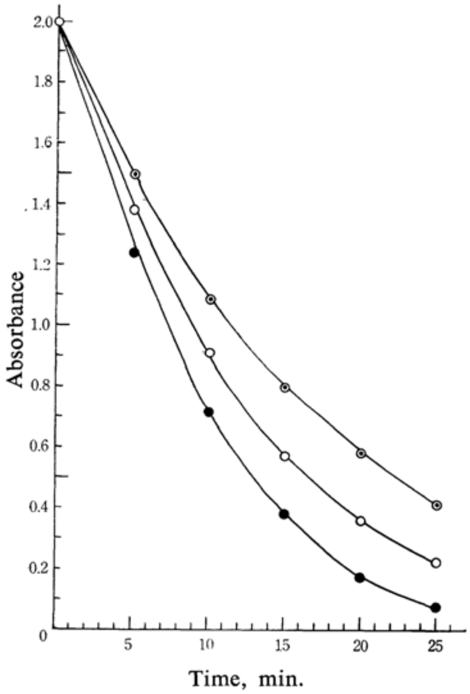

Fig. 2. Reaction rate curves.

30°C, Color reaction of FeSCN^{2+} is done by using 10 ml. of H_2O, 2 ml. of ferric solution and 1 ml. of $Hg(SCN)_2$ solution.

—●— 0.10 p. p. m. Br$^-$ (I)
—○— 0.02 p. p. m. Br$^-$ (II)
—⊙— Redistilled water (III)

Curves II and III in Fig. 2 were obtained by using a 0.02 p. p. m. bromide solution and redistilled water. As can be seen from Fig. 2, the reaction rate increased with an increase in the concentration of bromide, and the differences in absorbances among the three curves increased with the reaction time. These results indicate that the sensitivity of the method increases with the reaction time. However, in the solution with 0.10 p. p. m. bromide, the reaction has been almost completed after 25 min. and the sensitivity became small. A reaction time of 20 min. was adequate at 30°C.

The Amount of Iodide, the Reaction Time and the Temperature.—Curves I and II in Fig. 3 show the combined effect of the reaction time and the temperature. Similar calibration curves were obtained when shorter periods of time were used for higher temperatures.

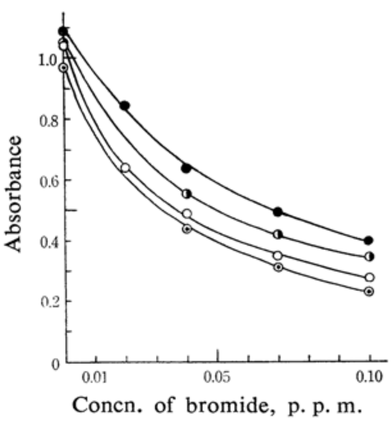

Fig. 3. Effects of reaction time, temperature and amounts of iodide.

—○— 30°C, 20 min., 1.5 ml. of iodide (I)
—●— 35°C, 10 min., 1.5 ml. of iodide (II)
—⊙— 30°C, 15 min., 1.0 ml. of iodide (III)
—◑— 30°C, 25 min., 2.0 ml. of iodide (IV)

The results with different amounts of iodide and different reaction times are shown by curves I, III and IV in Fig. 3. Similar curves were also obtained when longer periods of time were used for larger amounts of iodide. It was thought most favorable to use the reaction time of 20 min., the temperature of 30°C, and 1.5 ml. of the iodide solution.

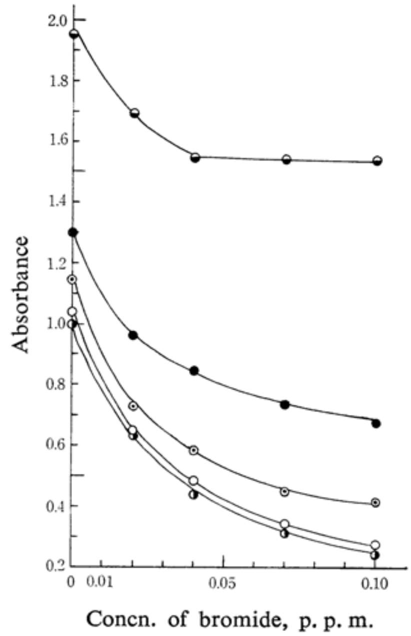

Fig. 4. Effect of amount of ceric solution. 30°C, 20 min., 0.2 M ceric solution is used.

—◒— 0.5 ml. —○— 2.0 ml.
—●— 1.0 ml. —◑— 2.5 ml.
—⊙— 1.5 ml.

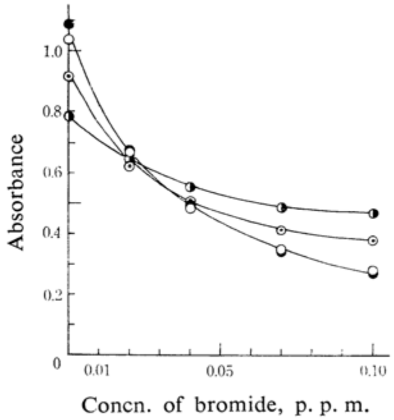

Fig. 5. Effect of amount of nitric acid. 30°C, 20 min., concentrated nitric acid is used.

—◑— 1.0 ml. —○— 2.0 ml.
—⊙— 1.5 ml. —●— 2.5 ml.

The Concentration of Reagents.—The effects of the ceric solution are shown in Fig. 4. The sensitivity increased with an increase in the amount of ceric solution added, but when more than 2.0 ml. of the ceric solution was used, no increase in sensitivity was obtained.

Figure 5 shows the effects of nitric acid. The larger the amount of nitric acid, the higher the absorbance of the blank solution and the lower that of the 0.10 p. p. m. bromide solution. However, by using 2.5 ml. of nitric acid, almost the same curve as that of 2.0 ml. was obtained. It appears that the nitric acid is necessary for this catalytic reaction. When sulfuric acid was used instead of nitric acid, no difference in absorbances between blank solution and 0.10 p. p. m. bromide solution was observed.

Dichromate is essential for this catalytic reaction. In its absence no difference in absorbance was obtained between blank and bromide solutions. In order to examine the

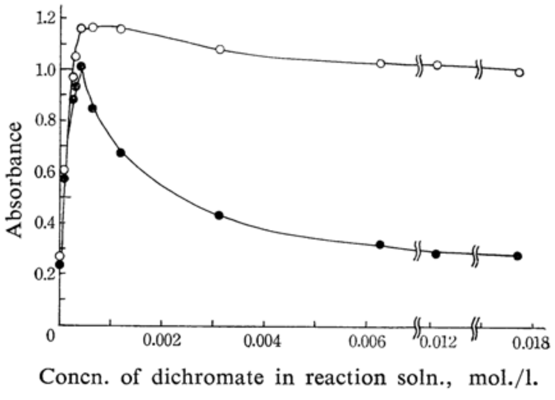

Fig. 6. Effect of concentration of dichromate. 30°C, 20 min.

—○— Redistilled water (I)
—●— 0.10 p. p. m. Br^- (II)

effects of dichromate, the reactions were performed in the presence of various amounts of dichromate using the blank solution and the solution containing 0.1 p. p. m. of bromide. The results are shown in Fig. 6. The presence of small amounts of dichromate caused a sharp decrease in the reaction rate and only a slight difference in absorbance between the two curves I and II. However, at higher concentrations than 0.0004 M in the reaction solution, curve II deviated remarkably from curve I with the increase in the concentration of dichromate; they then ran parallel to each other.

In order to ascertain the most suitable conditions, the effects of the amount of the dichromate solution were further determined, as shown in Fig. 7.

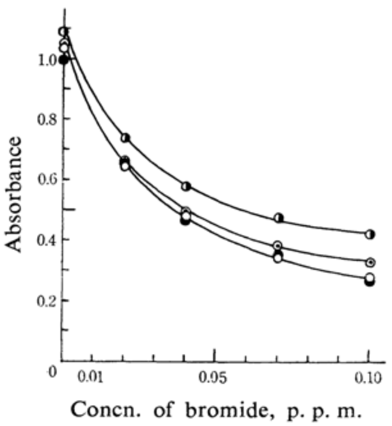

Fig. 7. Effect of amount of dichromate solution.
30°C, 20 min., 0.2 M dichromate solution is used.
—◑— 0.25 ml. —○— 1.0 ml.
—⊙— 0.5 ml. —●— 1.5 ml.

The sensitivity increased with an increase in the amount of dichromate solution added, but by using more than 1.0 ml. almost the same curves were obtained.

The Effect of Diverse Ions. — In order to make clear the effect of diverse ions on this method, some experiments were made in the presence of 0.04 p. p. m. of bromide ion and in its absence. The experimental results are given in Table I.

Nitrate and sulfate ions do not interfere at considerably high concentrations, but chloride ions interfere at 1 p. p. m. The effects of chloride ions will be described in detail in the following section. Iodide ions interfere slightly at 10 p. p. m. However, even if the sample contains more than 10 p. p. m. of iodide ions, the total amount of iodide in the reaction solution at the start of the oxidation can be

TABLE I. EFFECT OF DIVERSE IONS

Ion	Added as	Concn. p.p.m.	Absorbance Reagent blank	Absorbance 0.04 p. p. m. Br^-
None			1.061	0.509
			1.046	0.495
			1.041	0.478
NO_3^-	$NaNO_3$	62000 (1 M)	1.051	0.510
SO_4^{2-}	K_2SO_4	9600 (0.1 M)	1.215	0.791
		1000	1.061	0.507
CO_3^{2-}	Na_2CO_3	100	1.044	0.469
PO_4^{3-}	$Na_2HPO_4 \cdot H_2O$	10	1.044	0.507
F^-	NaF	100	1.086	0.585
		10	1.061	0.498
Cl^-	NaCl	1	0.951	0.471
I^-	KI	100	1.921	1.409
		10	1.086	0.541
ClO_3^-	$KClO_3$	10	1.032	0.478
IO_3^-	KIO_3	10	1.061	0.495
NO_2^-	$NaNO_2$	10	1.043	0.482
CN^-	KCN	10	0.770	0.376
		1	1.043	0.470
SCN^-	KSCN	10	0.772	0.367
		1	1.051	0.467
S^{2-}	$Na_2S \cdot 9H_2O$	10	1.096	0.545
		1	1.041	0.495
SO_3^{2-}	$Na_2SO_3 \cdot 7H_2O$	100	1.046	0.494
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	10	1.051	0.480
CrO_4^{2-}	K_2CrO_4	100	1.036	0.495
MnO_4^-	$KMnO_4$	1	0.801	0.388
		0.1	1.046	0.457
H_2O_2		100	1.046	0.465
Borate ion	H_3BO_3	10	1.032	0.479
Silicate ion (as SiO_2)		100	1.000	0.434
		50	1.036	0.509
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	100	1.046	0.476
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	100	1.046	0.488
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	100	1.046	0.478
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	100	1.035	0.478
Pb^{2+}	$Pb(NO_3)_2$	100	1.046	0.478
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	100	1.035	0.478
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	100	1.035	0.478
Co^{2+}	$CoSO_4 \cdot 7H_2O$	100	1.035	0.478
Cd^{2+}	$3CdSO_4 + 8H_2O$	100	1.035	0.478
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	100	1.046	0.509
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	100	0.959	0.456
Ce^{4+}	$Ce(SO_4)_2$	100	1.046	0.471
Mn^{2+}	$Mn(NO_3)_2 \cdot 6H_2O$	1	0.480	0.206
		0.1	0.932	0.431
Ag^+	Ag_2SO_4	0.1	0.883	0.367
		0.01	1.036	0.480
Hg^{2+}	$HgSO_4$	0.1	0.747	0.325
		0.01	1.046	0.495

kept at the constant concentration by decreasing the amount of the iodide reagent to be used. Permanganate and manganese(II) ions interfere at relatively low concentrations. Silver and mercuric ions interfere remarkably.

The Determination of Bromide in the Presence of Chloride.—This method is affected by 1 p.p.m. of chloride. As natural waters always contain small amounts of chloride, the effects of chloride were examined.

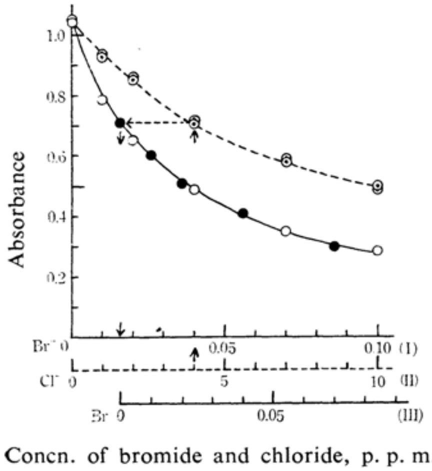

Fig. 8. Calibration curves.
30°C. 20 min.

—○— Br^- (I)
--⊙-- Cl^- (II)
—●— Br^- in the presence of 4 p. p. m. Cl^- (III)
←----- 4 p. p. m. Cl^- (↑) is equivalent to 0.016 p. p. m. Br^- (↓).

Curve II in Fig. 8 was obtained by this method by using standard chloride solutions of known concentrations. Curve I, the calibration curve of this method, is shown in Fig. 1. Chloride gives a curve similar to bromide when the concentrations of chloride are a hundred times larger than those of bromide. The experiments were also made by using standard bromide solutions containing 4 p. p. m. of chloride. The absorbances obtained are plotted against the concentrations of bromide on the abscissa III with solid circles. All these solid circles fall just on curve I. The concentration of bromide on the abscissa I minus that equivalent to 4 p. p. m. of chloride gives the value on the abscissa III. The same results were also obtained in the presence of different amounts of chloride. Thus, in samples containing small amounts of chloride, the concentration of bromide can be obtained by correcting the value for the chloride.

The concentration of chloride in the sample is first determined by the mercuric thiocyanate method.4) By means of curves I and II in Fig. 8, a concentration of bromide (*A* p. p. m.) equivalent to the concentration of chloride is obtained. Then the sample is treated by this method, and the value (*B* p. p. m.) is obtained by curve I. Thus, the concentration of bromide in the sample is calculated as the difference between *B* and *A* [$(B-A)$ p. p. m.].

The bromide contents in several natural waters were also determined by this method. The results are given in Table II.

TABLE II. DETERMINATION OF BROMIDE CONTENTS IN NATURAL WATERS

	Sample	Concn. of bromide p. p. m.	Concn. of chloride p. p. m.
No. 1	Rain water[*1] (I)	0.005	0.17
No. 2	River water[*2] (II)	0.070	16.2
No. 3	River water[*3] (III)	0.060	15.2
No. 4		0.062	
No. 5	Sample added bromide[*4]	0.082	

[*1] The sample was taken at Meguro-ku, Tokyo, July, 1963.

[*2] The sample was taken in River Tamagawa, Noborito-bashi, Tokyo, June, 1963.

[*3] The sample was taken in River Tamagawa, Futako-bashi, Tokyo, June, 1963.

[*4] The sample contains 0.020 p. p. m. of added bromide and 0.061 p. p. m. of originally present bromide.

Sample I was analyzed by using 10 ml., while samples II and III were analyzed by using samples diluted 3 ml. to 10 ml. The results given in Table II are calculated to original concentrations. The value listed in No. 4 was obtained by using sample III diluted 5 ml. to 10 ml. The comparison of the two results of sample III shows a good agreement. The method was also checked by adding a known amount of bromide to sample III. The determination of the total bromide concentration of this sample was made by using a sample diluted 3 ml. to 10 ml. The original concentration was calculated from the value thus obtained; it is listed in No. 5. This result shows that the known amount of bromide added is satisfactorily determined.

By this method, minute amounts of bromide in natural waters can be determined rapidly and sensitively.

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