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The Photometric Determination of Micro Amounts of Bromine in Silicate Rocks by Means of Its Catalytic Effect

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The catalytic action of bromide on the oxidation of to iodine iodate by potassium permanganate in sulfuric acid solution has been utilized for the microdetermination of bromine in silicate rocks. The method described consists of decomposing the silicate-rock sample by fusion with potassium hydroxide, leaching the melt with water, oxidizing bromide to bromine with potassium permanganate, extracting by benzene, and finally determining the bromine by the catalytic method. By this method, the bromine in samples with more than 0.04 ppm can be determined rapidly and accurately, using only 0.25—0.5 g of samples.

Data on the halogen contents of igneous rocks are important in discussing the relation between igneous rocks and magmatic emanations. The fluorine and chlorine contents have been reported by many investigators, but the data on bromine and iodine are rather scanty on account of the lack of a suitable analytical method. The results of a systematic investigation of bromine in rocks made by Behne[1] were long accepted as reliable, but the sensitivity of his analytical method (titrimetric) is too low to determine as low a bromine content as 1 ppm or less. In 1964, Filby[2] reported that the bromine content of two standard rocks collected by the U.S.Geological Survey, as determined by neutron activation analysis, was appreciably lower than Behne's average value. Recently, Sugiura[3] determined the bromine content of igneous rocks by a photometric method using rosaniline and molybdate after distillation. His values were also lower than those of Behne. Sugiura's method is applicable to rocks with more than 0.2 ppm bromine, but its sensitivity is not yet enough for many igneous rocks.

The sensitivities of usual photometric methods are too low for them to be used in the determination of bromine in igneous rocks. The neutron activation method has, indeed, a very high sensitivity, but it requires special equipment and time-consuming irradiation procedures.

One of the present authors (I.I.) and others[4] have previously reported a photometric method for the determination of bromide, a method based on the catalytic effect of bromide on the oxidation of iodine to iodate by potassium permanganate in a sulfuric acid solution. This method has an excellent sensitivity and sufficient accuracy and does not need any expensive equipment.

The present authors have first investigated in detail the iodine-potassium permanganate reaction in the presence of Br^- or Cl^- as a catalyst and have established optimum conditions for the microdetermination of bromine by means of its catalytic effect.

Although the catalytic action itself is highly selective, the method is affected by various coexisting substances. Because of the chemical complexity of usual silicate rocks, the isolation of bromine is necessary before using the catalytic method. We have established a rapid, sensitive, and accurate method for the determination of very small amounts of bromine ($>$0.04 ppm) in common silicate rocks.

Experimental

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

The reactions were carried out in a water bath kept at 25.0±0.1°C with a Taiyo Thermo Unit.

Reagents. All the chemicals used were of analytical-reagent quality. Redistilled water was used for the reagent preparation and throughout the procedure.

Potassium Iodide Solution. Dissolve 1.31 g of potassium iodide and 2 g of sodium carbonate in water and dilute to 1 *l*; this yields 1 mg/m*l*.

*Potassium Permanganate Solution (0.04*M*).*

Potassium Bromide Solution. Prepare a 0.1 M potassium bromide solution. The solution is standardized by Volhard's method.[5] Prepare the working solution by

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[1] W. Behne, *Geochim. Cosmochim. Acta*, **3**, 186 (1953).

[2] R. H. Filby, *Anal. Chim. Acta*, **31**, 434 (1964).

[3] T. Sugiura, This Bulletin, **41**, 1133 (1968).

[4] M. Shiota, S. Utsumi and I. Iwasaki, *Nippon Kagaku Zasshi*, **80**, 753 (1959).

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

diluting this solution adequately.

Sodium Chloride Solution. Dissolve 1.649 g of sodium chloride in water and dilute to exactly 1 *l*. This solution contains 1 mg of chloride per m*l*. The working solution is prepared by successive dilutions.

Sulfuric Acid Solution (1 : 1).

Ferric Ammonium Sulfate Solution. Dissolve 6 g of ferric ammonium sulfate in 100 m*l* of a 6 N nitric acid solution. The solution is then stored in a brown glass bottle.

Mercuric Thiocyanate Solution. Solid mercuric thiocyanate was prepared as has been described by Utsumi.[6] Dissolve 0.3 g of mercuric thiocyanate in 100 m*l* of absolute ethyl alcohol.

Sodium Sulfite Solution (0.1 M). Dissolve 1.26 g of anhydrous sodium sulfite in 100 m*l* of water. This solution is prepared afresh each week.

Potassium Dichromate Solution (0.01 M).

Benzene. Wash guaranteed benzene with a 1 N sodium hydroxide solution, a 1 N sulfuric acid solution, and finally three times with water.

Procedure and Calibration Curve. 0.25 to 0.5 g of a finely-powdered sample is placed in a 30-m*l* nickel crucible. Add 3.0 g of potassium hydroxide pellets to the crucible. Cover the crucible, and heat it to about 500°C on an electric heater for 15 min. Leach the resulting fused cake with 35 m*l* of water. Centrifuge the resulting suspension in a 50-m*l* centrifuge tube. Transfer the supernatant liquid to a 100-m*l* separatory funnel. Add 10 m*l* of water to the residue, shake, and centrifuge again. Transfer the supernatant liquid to the above-mentioned separatory funnel.

To the solution in the separatory funnel add 1.5 m*l* of the sodium sulfite solution, and then 6.4 m*l* of the sulfuric acid solution (1 : 1).

After the solution has stood for about 10 min, add the potassium dichromate solution until the yellow color of the dichromate ion persists. After the subsequent addition of 30 m*l* of benzene, immerse the separatory funnel in a water bath kept at 25°C for about 15 min. Start shaking (360 strokes/min, using a shaker) immediately after adding 1.2 m*l* of the potassium permanganate solution. After 20 min's shaking, discard the aqueous layer. Shake the organic layer with 5 m*l* of 1.8 N sulfuric acid for one minute. Discard the aqueous phase. To the organic layer, add 3.0 m*l* of a 1 N sodium hydroxide solution and 16.8 m*l* of water, and shake the separatory funnel for 3 min. After the phase separation, transfer the aqueous layer to a 50-m*l* separatory funnel. Care must be exercised to completely exclude benzene, since even a small amount of benzene disturbs the subsequent procedure.

To the aqueous layer, add 3.2 m*l* of the sulfuric acid solution (1 : 1) and 1.0 m*l* of the potassium iodide solution, and then mix. Place the separatory funnel in a water bath at 25.0±0.1°C for about 15 min. Start the reaction by adding 0.5 m*l* of the potassium permanganate solution (at the same temperature). Swirl to mix thoroughly and let the separatory funnel stand in the water bath. Exactly 3 min after the addition of the potassium permanganate solution, add 10 m*l* of cold (about 0°C) carbon tetrachloride and immediately shake the separatory funnel for 15 sec.

After the phase separation, transfer the organic layer to a 50-m*l* separatory funnel. To the organic layer, add 10.0 m*l* of water, 2.0 m*l* of the ferric ammonium sulfate solution, and 1.0 m*l* of the mercuric thiocyanate solution, and shake the separatory funnel for about one minute. The aqueous layer is thus colored with ferric thiocyanate. Measure the absorbance of this aqueous layer at 460 $m\mu$ using a 10-mm cell and against water used as a reference.

The calibration curve shown in Fig. 1 was obtained by the procedure described above, using 45 m*l* of standard bromide solutions (or bromate solutions) of known concentrations and 3 g of solid potassium hydroxide.

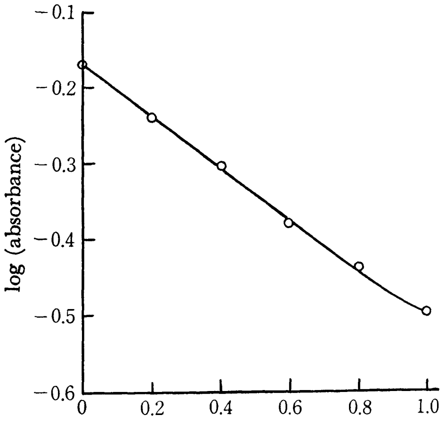

Fig. 1. Calibration curve.

Results and Discussion

The Catalyzed Oxidation Reaction of Iodine by Permanganate. The oxidation reaction between iodide and potassium permanganate in an acid medium is shown in Eqs. (1) and (2).

$$10\,I^- + 2MnO_4^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O \qquad (1)$$

$$I_2 + 2MnO_4^- + 4H^+ \xrightarrow[\text{catalyst}]{Br^-,\ Cl^-} 2IO_3^- + 2Mn^{2+} + 2H_2O \qquad (2)$$

The reaction (1) is very fast compared to the reaction (2), which is the rate-determining step. The rate of the reaction (2) was followed by the photometric determination of the change in the concentration of the unreacted iodine as a function of the time.

One of the present authors (I.I.) and others[7] have previously reported a photometric method for the determination of iodide by using ferric ammonium sulfate and mercuric thiocyanate. In order to examine the relationship between the amounts of unreacted iodine and the absorbance, a series of reaction mixtures containing various amounts of iodine was prepared. Into each separatory funnel, 20-m*l* portions of iodide solutions of known con-

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[6] S. Utsumi, *Nippon Kagaku Zasshi*, **73**, 835 (1952).

[7] I. Iwasaki, S. Utsumi, A. Tomonari and I. Morita, *ibid.*, **80**, 749 (1959).

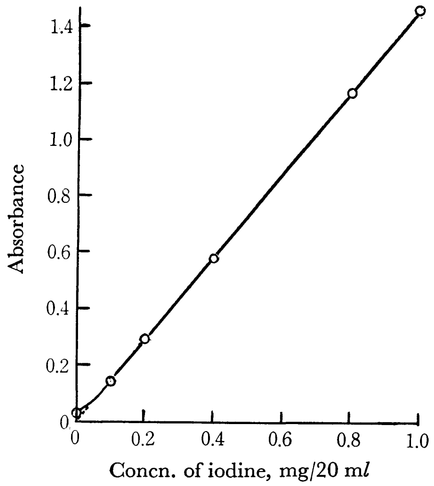

Fig. 2. Relationship between concentration of iodine and absorbance at 460 mμ.

centrations, 3 m*l* of sulfuric acid (1 : 1), and 3 m*l* of a 3% hydrogen peroxide solution were introduced. The resulting iodine was extracted with 10 m*l* of carbon tetrachloride and was colored with ferric thiocyanate as in the analytical procedure.

As is shown in Fig. 2, there is a linear relationship between the absorbance at 460 mμ and the concentration of iodine, but not at low concentrations. In order to exclude the nonlinear portion of the curve, absorbance readings were subsequently confined to the range of from 0.1 to 1 mg of iodine.

The concentration of sulfuric acid suitable for the oxidation reaction was first sought. The reaction proceeds smoothly when 3 m*l* of the sulfuric acid solution (1 : 1) are added to 20 m*l* of a sample.

After the most satisfactory conditions of acidity had been determined, the effect of potassium permanganate on the oxidation reaction in the absence of bromide or chloride was investigated by adding 0.5-m*l* portions of potassium permanganate solutions with various concentrations.

The plots of the log absorbance *vs.* the time yield fairly good straight lines, indicating a first order relationship with respect to iodine. From the slopes of the straight lines, the rate constants, *K*, were calculated; they were then plotted as a function of the initial concentration of potassium permanganate (Fig. 3). The direct proportionalities between the rate constants and the initial concentration of potassium permanganate indicate that the reaction is again first order with respect to potassium permanganate. (Variations in the ionic strength in this range produce no effect on the reaction rate; the rate did not change even in the presence of 0.1 mol/*l* of sodium sulfate).

The reaction rate increases sharply with an increase in the concentration of potassium permanganate, as is shown in Fig. 3. Consequently, the higher the concentration of potassium permanganate, the lower the accuracy of the present kinetic method because of the inevitable variation in the rate of the noncatalytic reaction. It is best to use 0.5 m*l* of a 0.04M potassium permanganate solution, because the reaction proceeds relatively slowly under these conditions.

The catalyst may influence the rate constant without altering the kinetic order of the noncatalytic reaction. Accordingly, using solutions containing bromide or chloride we carried out catalyzed reactions between iodine and potassium permanganate with 0.5 m*l* of a 0.04M potassium permanganate solution.

The reaction rate curves, II, III, and IV, in Fig. 4 were obtained by using 0.02- and 0.05-ppm bromide solutions and a 5-ppm chloride solution. The curve I was obtained by using redistilled water. The differences in absorbances among the three curves (I, II, and III) are largest after 3 minutes. A reaction time of 3 min is adequate for

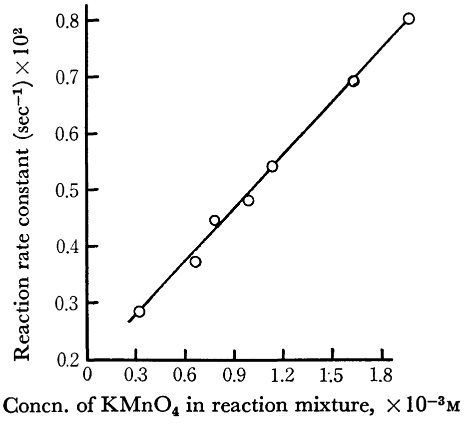

Fig. 3. Effect of potassium permanganate on the reaction rate constant.

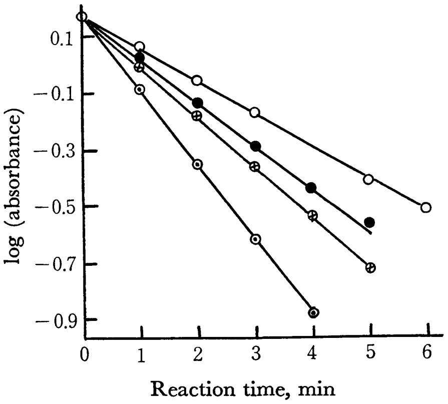

Fig. 4. Effects of bromide and chloride on the reaction rate.

○ redistilled water (I) ⊗ 0.02 ppm Br$^-$ (II) ⊙ 0.05 ppm Br$^-$ (III) ● 5 ppm Cl$^-$ (IV) the determination of bromide because of the high sensitivity. As can be seen in Fig. 4, the reaction follows approximately (pseudo) first order kinetics at each catalyst concentration, and the first order rate constant increases with the quantity of the catalyst. If the reaction is first order with respect to the catalyst, for the same initial concentration of potassium permanganate the log absorbance and the catalyst concentration should yield a linear relationship at a constant reaction time.

In order to confirm this point, experiments on a series of reaction mixtures containing various amounts of catalysts were carried out. In Fig. 5, the resulting log absorbance are plotted against the catalyst concentration. At a low concentration of the catalyst, the linear relationship was recognized, but at a high concentration there was a departure from linearity. It seems that the catalyst dependence is first order at a low concentration. The catalytic effect of chloride is smaller than that of bromide. The abundance of chlorine in silicate rocks is, however, considerably greater than that of bromine.

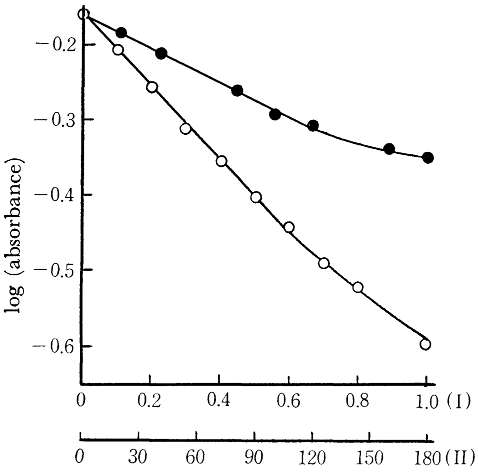

Fig. 5. Effects of amounts of bromide and chloride.
○ Br^- (I) ● Cl^- (II)

Extraction. Utsumi *et al.*[8] have discussed the extraction of small amounts of bromine (order of 100 μg) by carbon tetrachloride in the determination of bromide in natural waters. Their procedure was based on the selective oxidation of bromide to bromine by potassium permanganate. In this investigation the present authors examined the extraction procedure of less than 1 μg of bromine. Bromide was oxidized to bromine by employing various oxidizing agents. The resulting bromine was extracted by benzene, stripped from the organic layer by a sodium hydroxide solution, and determined by the catalytic method. The use of carbon tetrachloride as the solvent was not suitable, because a minute amount of carbon tetrachloride retained in the aqueous layer remarkably promoted the iodine-potassium permanganate reaction in the subsequent procedure.

It was found that the oxidation of bromide to bromine by potassium dichromate or ceric ammonium sulfate is very slow and that the oxidation reaction by potassium permanganate proceeds fairly smoothly. However, the recovery of added bromide decreased with an increase in the standing time for the oxidation by permanganate, and satisfactory results were not obtained.

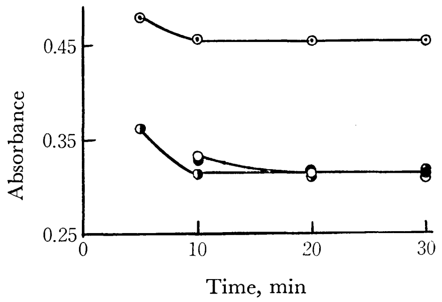

Fig. 6. Effect of shaking time on oxidation and extraction.
25°C, Volume of sample solution: 50 m*l*
○ 18N H_2SO_4 2 m*l*, Br^- 1 μg
◑ 18N H_2SO_4 4 m*l*, Br^- 1 μg
0.04M $KMnO_4$ 1 m*l*
● 18N H_2SO_4 6.4 m*l*, Br^- 1 μg, KOH 3 g
⊙ 18N H_2SO_4 6.4 m*l*, Br^- 0.5 μg, KOH 3 g
0.04M $KMnO_4$ 1.2 m*l*

TABLE 1. RECOVERY OF ADDED BROMIDE AFTER EXTRACTION

Br^- added, μg	0.20	0.40	0.60	0.80	1.00
Br^- found, μg	0.14	0.28	0.43	0.57	0.71
Recovery, %	70	70	72	71	71

Subsequently, the oxidation of bromide to bromine by permanganate and the extraction of the resulting bromine by benzene were made simultaneously. The extraction was carried out at 360 strokes/min using a shaker. As can be seen in Fig. 6, the absorbance at first changes rapidly with the shaking time, and then, after about 20 min, it does not change very much. In order to ascertain the recovery of added bromide after oxidation and extraction, some experiments were made using solutions containing various quantities of bromide.

The results listed in Table 1 show that recovery is about 70%, regardless of the amount of bromide. It was also found that the recovery of bromide increases slightly with an increase in the shaking

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[8] I. Iwasaki, S. Utsumi, I. Morita and M. Shiota, *nippon Kagaku Zasshi*, **80**, 744 (1959).

Table 2. Effect of diverse ions

Ion	Added as	Amount µg	Absorbance: Reagent blank	Absorbance: 0.6 µg Br^-
None			0.681	0.420
Fe^{3+}	$Fe_2(SO_4)_3(NH_4)_2SO_4\cdot 24H_2O$	10^5	0.680	0.422
Mg^{2+}	$MgSO_4\cdot 7H_2O$	5×10^4	0.685	0.420
Al^{3+}	$K_2Al_2(SO_4)_4\cdot 24H_2O$	5×10^4	0.680	0.420
Silicate ion	SiO_2+KOH	4×10^5	0.675	0.423
Cl^-	NaCl	3×10^2	0.680	0.420
		5×10^2	0.672	0.416
		10^3	0.650	0.405
Hg^{2+}	$HgSO_4$	1	0.678	0.422
		2	0.689	0.465
		10	—	0.420*
Ag^+	Ag_2SO_4	5	0.685	0.425
		10	0.685	0.450
I^-	KI	40	0.690	0.421

* The procedure of potassium hydroxide fusion was carried out.

rate. Even when bromine once extracted into benzene is shaken with a washing solution of 1.8N sulfuric acid, appreciable amounts of bromine do not move to the aqueous layer. Bromine extracted in benzene is stripped into the aqueous layer by shaking it for about 2 min with a sodium hydroxide solution.

The Effect of Diverse Ions. The effect of diverse ions on this method was studied, some experiments being made in the presence of 0.6 µg of bromide and in its absence. The experimental results given in Table 2 were obtained without fusion. Magnesium, iron, aluminum, and silicate do not interfere, even at high concentrations. Chloride interferes slightly at 500 µg. However, even if the sample contains a large amount of chloride, the bromine can be determined by decreasing amounts of the sample to be weighed, for fortunately, the bromine-to-chlorine ratios in igneous rocks are rather constant.3),*1 Iodide does not interfere at 40 µg. As silver and mercuric ions react with bromide, they interfere even at low concentrations. However, the interference of mercury can be completely removed by fusion with potassium hydroxide. Most igneous rocks do not contain silver in concentrations which cause any serious interference.9,10)

Table 3. Determination of bromine in some silicate rocks

Sample	Amount of sample, g	Br added µg	Br found µg		Br found in washed residue µg	Concn. of Br ppm (Average)
I (Basalt)	0.5	—	0.82	0.84	(0.00)	1.66
II (Andesite)	0.5	—	0.71	0.78	(0.01)	
			0.73	0.71	(0.00)	1.45
			0.70			
	0.25	—	0.36	0.35		
			0.37	0.40		1.48
	0.25	0.50	0.85	0.85		
III (Liparite)	0.25	—	0.64	0.63	(0.02)	
			0.61		(0.01)	2.51
	0.25	0.30	0.90	0.93		

[*1] The results of the determination of bromine and other halogens in igneous rocks will be reported in a forthcoming paper.

9) K. Rankama and Th. G. Sahama, "Geochemistry," University of Chicago Press, Chicago (1950), p. 702.

10) M. Fleischer, *Geochim. Cosmochim. Acta*, **29**, 1263 (1965).

In practice, many metal ions occurring in silicate rocks are removed as precipitates by potassium hydroxide fusion. The amounts of bromine retained in the washed residue of fused silicate rock samples is small enough to be neglected. The amounts of bromine found in the washed residue are given in Table 3. These results were obtained by dissolving the washed residue with sulfuric acid (1.8N) and sodium sulfite solutions and using the method described under "Procedure and Calibration Curve."

The Results of Determination. The reproducibility of the method was tested by taking 0.25 to 0.5-g samples of various silicate rock samples and by then following the procedure described above. The method was also checked by adding known amounts of bromide to rock samples. The results shown in Table 3 demonstrate the reliability of the method.

According to these results, it may be concluded that the present method is satisfactory for the determination of bromine in rocks. By this method, bromine in samples with more than 0.04 ppm can be determined rapidly using only 0.25 to 0.5-g portions of the sample. The error in this method is about ±0.03 μg at bromine of 0.50 μg and less at lower amounts.

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