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The Photometric Determination of Minute Amounts of Iodine in Silicate Rocks[*1]

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A rapid and sensitive method for the determination of minute amounts of iodine in silicate rocks has been developed. A rock was fused with potassium hydroxide, and the cake was treated with water and sulfuric acid. The iodine in the solution was reduced to iodide by sodium sulfite, and was then oxidized to free iodine by sodium nitrite. The free iodine thus obtained was extracted with carbon tetrachloride and then back-extracted with a sodium hydroxide solution. The iodine in this aqueous layer was determined photometrically by a method based on the catalytic effect of iodine on the color-fading of ferric thiocyanate. By the proposed method, amounts of iodine as low as 0.007 μg in a 1-g sample of silicate rocks can be determined. Application to some igneous rock samples gave results with a relative standard deviation of less than 7.2%, except for very low concentrations.

Since von Fellenberg's classical work,1) there have been almost no data on iodine in rocks. Recent determinations of iodine in meteorites by neutron-activation analysis suggest, however, that the iodine contents of rocks may be much smaller than those reported by von Fellenberg. Therefore, reliable data on iodine in rocks are desirable from the viewpoint of geochemistry. However, the determination of iodine in rocks requires an extremely sensitive method, for the iodine content in rocks is very low, particularly in igneous rocks.

Crouch2) has developed a spectrophotometric method for determining the iodine in silicate rocks based on the starch-iodine reaction, but this method requires quite a large sample and a time-consuming procedure; there are also some problems still to investigate regarding the treatment of the residue resulting from the dissolution of rocks. The kinetic method,3) followed by titration, is also not sensitive enough to analyse iodine in igneous rocks. Goles and Anders4) have determined the iodine contents of some meteorites by neutron-activation analysis. Recently, Tajima and Akaiwa5) have reported a method of determining the iodine in sedimentary rocks, also by neutron-activation analysis. These methods may be suitable in sensitivity, but their procedures are time-consuming and require considerable manipulation and special equipment.

Yonehara and others6–8) have previously reported colorimetric methods for the determination of ultramicro amounts of iodine by utilizing its catalytic effect on the color-fading of ferric thiocyanate. According to these methods, 0.005 μg of iodine can be determined colorimetrically. Although the catalytic method is very sensitive, it is supposed that there are some difficulties in the separation of iodine from rocks because of the chemical complexity of silicate rocks and the very low content of iodine. After a rock had been decomposed by fusion, we tried to separate the iodine as follows. As the iodine in the solution obtained by dissolving the cake is presumably in a highly oxidized form, such as the iodate ion, iodate was first reduced to iodide by sodium sulfite. The iodide was then oxidized to free iodine by sodium nitrite. The free iodine was extracted with carbon tetrachloride, and then back-extracted with a sodium hydroxide solution. Finally the iodine in the aqueous layer was determined by the catalytic method.

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According to a previous study,[9] the iodine content in igneous rocks seems to be less than 0.1 μg/g; therefore, a 0.5–1-g sample of silicate rocks is required for the application of the catalytic method to the determination of iodine in rocks. The treatment of the cake obtained by the fusion of a 1-g rock sample requires considerable amounts of water, causing the solution finally obtained to have an extremely low iodine concentration. That the behavior of very small amounts of iodine differs significantly from that of macro amounts of iodine[10,11] suggests the difficulty of achieving the quantitative separation of iodine in low concentrations such as that discussed above.

In the present work, we investigated whether the separation processes involving reduction, oxidation, extraction, and back-extraction could be performed quantitatively at very low concentrations and whether the catalytic method could be applied to the determination of iodine in silicate rocks. In addition, the catalytic method was modified so as to increase the sensitivity by changing the concentration of the reagents and the conditions of the reaction.

Experimental

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

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

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

Redistilled water was used for the reagent preparation and throughout the procedures.

(Treatment of Rocks)

Potassium Hydroxide. The potassium hydroxide used for the fusion of rocks was a special-grade reagent; SV grade, obtained from the Tokyo Ôka Kôgyo Co., Ltd.

Sulfuric Acid Solution (1 : 1).

Sodium Sulfite Solution (about 5%).

Sodium Nitrite Solution (1.0M). Dissolve 6.90 g of sodium nitrite in water and dilute to 100 m*l*.

Sodium Hydroxide Solution (0.1N). Dissolve 2.0 g of sodium hydroxide in water and dilute to 500 m*l*.

(The Catalytic Reaction)

Ferric Ammonium Sulfate-Nitric Acid Solution. Dissolve 6 g of ferric ammonium sulfate in 100 m*l* of a 7.0N nitric acid solution.

Potassium Thiocyanate Solution (0.010M). Diluted from about a 0.1M potassium thiocyanate solution, as standardized by Volhard's method.

Sodium Nitrite Solution (0.014M). Dissolve 0.483 g of sodium nitrite in water and dilute to 500 m*l* in a volumetric flask.

Sodium Chloride Solution (20 g of Chloride per l). Dissolve 32.971 g of sodium chloride in water and dilute to exactly 1*l*.

Standard Iodide Solution. Prepare about a 0.1M potassium iodide solution and standardize by Volhard's method. Prepare the working solutions by diluting this solution adequately.

Standard Iodate Solution. Dissolve 0.847 g of potassium iodate in water and dilute to exactly 500 m*l* to give an iodine concentration of 1000 ppm. Prepare the working solutions by successive dilutions.

Procedure and Calibration Curve. Into a 30-m*l* nickel crucible, add 0.5—1 g of the powdered rock sample and the flux (potassium hydroxide, about six times the weight of the rock sample); heat first over a small flame, gradually raise the temperature to about 500°C, and then heat further for about 30 min. After cooling to room temperature, dissolve the cake with 15—20 m*l* of water and transfer all of the contents to a 50-m*l* centrifuge tube with a glass stopper. Crush the cake with a glass rod and stir the solution to dissolve the soluble material. After the solution has been centrifuged at about 3000 rpm for 5 min, transfer the supernatant liquid to a 50-m*l* glass beaker. Add a 1 : 1 sulfuric acid solution to neutralize the solution, and then add an excess of 1 m*l* of the acid. Then add 0.3 m*l* of a 5% sodium sulfite solution.

Into the centrifuge tube containing the residue, add 10 m*l* of water, 1—2 m*l* of the 1 : 1 sulfuric acid solution, and 0.1 m*l* of the 5% sodium sulfite solution, and shake vigorously to dissolve the residue. It is desirable to use just the amounts of sulfuric acid necessary to dissolve the residue present. Almost all of the precipitate can be dissolved by this procedure. Centrifuge again and pour the supernatant liquid into the same beaker. Wash the remaining residue three times with 2 or 3 m*l* of redistilled water and small portions of the 1 : 1 sulfuric acid, and pour all of the washings into the beaker. Keep the total volume of the 1 : 1 sulfuric acid used in washing at 1 m*l*. Transfer the solution thus obtained into a 100-m*l* separatory funnel and bring the volume of the solution to 60—80 m*l*. Then add 3.0 m*l* of a 1M sodium nitrite solution, mix thoroughly, add 10 m*l* of carbon tetrachloride, and shake the separatory funnel for 1 min. After the layers have

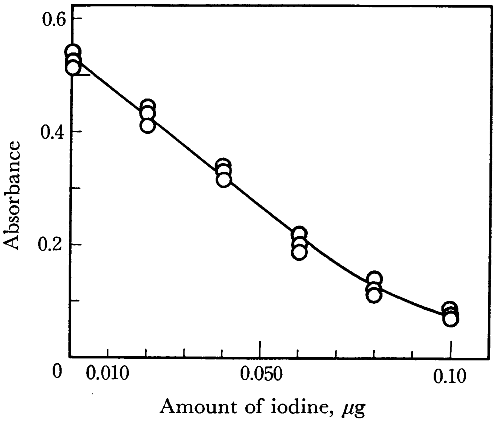

Fig. 1. Calibration curve.

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TABLE 1. CONTAMINATION DURING FUSION PROCESS

	Absorbacne				
					Mean
Without fusion*	0.509	0.533	0.539	0.553	0.534
Heated for 1.5 hr**	0.523	0.527	0.542	0.551	0.536
Heated for 3 hr**	0.461	0.526	0.544	0.565	0.519

5 g KOH was used.

* obtained by following the procedure without fusion.

** obtained by the procedure.

been completely separated, transfer the carbon tetrachloride phase into a 50-m*l* separatory funnel.

When a large amount of the residue still remains, dissolve this residue with 60—80 m*l* of water, 2 m*l* of the 1 : 1 sulfuric acid solution, and 0.3 m*l* of the 5% sodium sulfite solution, and then determine the iodine in this solution separately. Add the value obtained to that of the supernatant liquid obtained above.

To the carbon tetrachloride phase thus obtained, add 8.0 m*l* of water, 1.0 m*l* of a 0.1N sodium hydroxide solution, and 1.0 m*l* of a sodium chloride solution (2.0% as chloride), shake the separatory funnel for 1 min, and allow the layers to separate. Then transfer the aqueous layer into a 20-m*l* glass tube with a glass stopper. The iodine in this aqueous phase is then determined by the following catalytic method.

To the solution in the glass tube, add 1.0 m*l* of a 0.014M sodium nitrite solution and 1.0 m*l* of a 0.010M potassium thiocyanate solution, and mix thoroughly. Place the glass tube in a water bath at 60°C for about 10 min. Start the reaction by adding 3.0 m*l* of a nitric acid solution of ferric ammonium sulfate (at the same temperature), and then replace the glass tube in the water bath. Exactly 18 min after the addition of the ferric ammonium sulfate solution, measure the absorbance of the solution at 460 mμ, using water as the reference.

The calibration curve shown in Fig. 1 was prepared by taking 0.0-, 2.0-, 4.0-, 6.0-, 8.0- and 10.0-m*l* aliquot of a 0.010 ppm standard iodate solution and 1—6 g of potassium hydroxide, and by then following the procedure described above without fusion. The variation in sensitivity and in absorbance values resulting from the use of different batches of reagents makes it necessary to check the calibration curve for each set of determinations.

Results and Discussion

The Treatment of Rocks. In order to determine the iodine in rocks, decomposition and separation procedures must be used. In the present work, the fusion with potassium hydroxide was adopted, because this fusion is made at a relatively low temperature and a specially-pure reagent is obtainable. The use of sodium hydroxide gave lower absorbances than those of potassium hydroxide.

When the cake was treated with water, iodine was distributed to both the aqueous phase and the residue. As the iodine in the residue could not be removed to the aqueous phase by washing, it was necessary to dissolve the residue with sulfuric acid and to combine the resultant solution with the aqueous phase obtained above.

Decomposition by hydrofluoric acid was not adaptable because of the volatilization of the iodine during the process.

The Contamination during the Fusion Process. In order to examine the possibility of contamination during a fusion process, absorbances were measured by following the above procedure, after a 5-g portion of potassium hydroxide had been fused in the absence of iodine. The values without fusion were also obtained. As the comparison of these values shows good agreement, as can be seen in Table 1, the contamination during the fusion process was found to be insignificant.

The Reduction of Iodate to Iodide. Several experiments were made to examine the reduction of iodate to iodide by using a 5% sodium sulfite solution. In order to obtain a tolerable reproducibility of the reduction of the minute amounts of iodate,

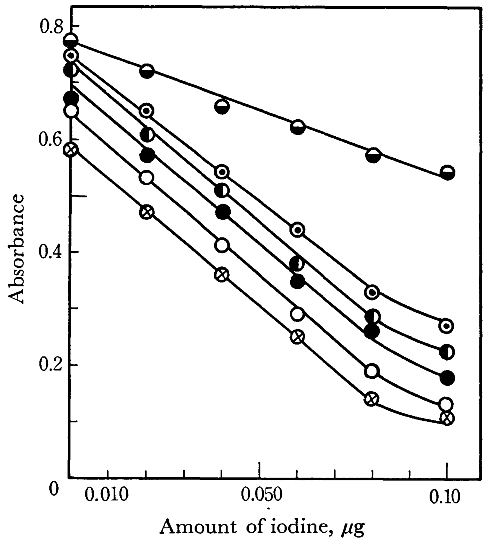

Fig. 2. Effect of amount of nitrite solution. (in the absence of KOH)
1M nitrite solution is used.

—◓— 0.1 m*l*
—⊙— 0.5 m*l*
—◐— 1.0 m*l*
—●— 2.0 m*l*
—○— 3.0 m*l*
—⊗— 4.0 m*l*

less than 0.10 μg as iodine, it was necessary to keep the volume of the solution less than 50 m*l* at the reduction. As the reduction time, more than 15 min was required. No effect was observed on varying the volume of the sodium sulfite solution added.

The Oxidation of Iodide to Free Iodine. In measuring the effect of the amount of sodium nitrite on the oxidation of iodide, several experiments were made using a 1.0M sodium nitrite solution and the procedure featuring the absence of potassium hydroxide. The experimental results are shown in Fig. 2. The effect of the volume of the solution on the oxidation was examined; the same calibration curves were obtained on the volumes of 50, 60, and 80 m*l*.

The Use of Sulfuric Acid. In most cases of rock analysis, the rock samples are treated with hydrochloric acid. However, in this work, reduction, oxidation, extraction and back-extraction were not achieved quantitatively by using hydrochloric acid. Therefore, sulfuric acid was used. As can be seen in Fig. 3, the effect of the amount of sulfuric acid added is quite similar to that of sodium nitrite.

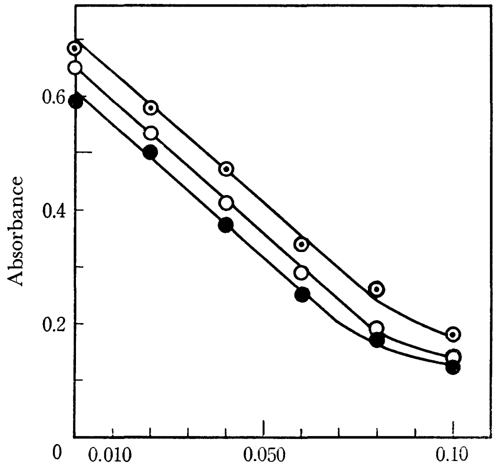

Fig. 3. Effect of amount of sulfuric acid.
(in the absence of KOH)
1 : 1 sulfuric acid is used.
—⊙— 1.0 m*l* —○— 2.0 m*l*
—●— 3.0 m*l*

The Extraction and the Back-Extraction. In order to treat the cake obtained by the fusion of a 1-g rock sample, it is desirable to use 200 m*l* of water. The extraction of iodine from 200 m*l* of the solution was first attempted; however, the results obtained were not reproducible enough to determine the iodine. It was necessary to keep the volume of the solution within 80 m*l*. The reproducibility deteriorated slightly when the shaking time was less than 30 sec.

Ten milliliters of a sodium hydroxide solution convenient for the subsequent catalytic method were used. The use of a concentration of 0.005—0.1N gave the same recovery of iodine. The effect of the presence of chloride has been described in previous papers.[7,8)]

The Effects of the Amounts of Potassium Hydroxide and Silicate. As considerable amounts of potassium ion and silicate ion are introduced into the solution by the fusion of silicate rocks, the effects of their amounts were examined. The experiments were made using 1–6 g of potassium hydroxide and the procedure without fusion. All of the values obtained fell just on the curve shown in Fig. 1. A 250—700-mg portion of silica was fused with 3 or 6 g of potassium hydroxide and a known amount of iodate was added; the same results were obtained. When the solution contains a considerable amount of the silicate ion, the precipitate of silica appears on neutralization. However, the presence of the precipitate in the solution does not disturb the subsequent procedure.

The Effect of Diverse Ions. To examine the effect of the substances commonly occurring in igneous rocks, several experiments were made in the presence of 0.06 and 0.04 μg of iodate and in its absence. The quantities of these substances studied may be the maximum content present in 1 g of common igneous rocks. There appears to be no significant effect of these substances, as is shown in Table 2.

TABLE 2. EFFECT OF DIVERSE IONS

Ion	Amount added mg	Iodine taken μg	Iodine found μg
Fe^{3+}	100	0.000	0.000
		0.040	0.038
		0.060	0.057
Al^{3+}	130	0.000	0.006
		0.040	0.031
		0.060	0.057
Mg^{2+}	80	0.000	0.000
		0.040	0.039
		0.060	0.058
Ca^{2+}	70	0.000	0.006
		0.040	0.043
		0.060	0.061
Mixture		0.000	0.000
Fe^{3+}	50	0.040	0.043
Al^{3+}	70	0.060	0.056
Ca^{2+}	45		
Silicate ion	535		
KOH	6000		

The Determination of Iodine in Rocks. The iodine in several igneous rocks was determined by the present method; the results are shown in Table 3. The determinations were made by taking 1-g and 0.5-g samples; the results show good agreement

TABLE 3. DETERMINATION OF IODINE IN SILICATE ROCKS

Sample		Iodine found					Mean	Std.	Relative
Name and locality	Weight g	μg/g					μg/g	devn.	std. devn. %
Basalt									
1950—1951 lava	0.500	0.084	0.088	0.084	0.084	0.082	0.082	0.0059	7.2
O-sima,	1.00	0.075	0.075	0.074	0.085	—			
Tokyo, Metr.									
Andesite									
1946 lava	0.500	0.046	0.040	—	—	—	0.042	0.0027	6.4
Sakura-zima,	1.00	0.044	0.040	0.041	—	—			
Kagosima Pref.									
Obsidian									
Sirataki,	0.500	0.016	0.016	0.022	—	—	0.020	0.0034	17
Hokkaido	1.00	0.022	0.020	0.024	—	—			

TABLE 4. RECOVERY OF IODINE FROM FUSION PROCESS

	Sample Weight g	Iodine from rock μg	Iodine added μg	Total iodine μg	Iodine found μg	Error %
No. 1	1.00	0.082	0.047	0.129	0.121	−6.6
	0.500	0.041	0.047	0.088	0.086	−2.3
No. 2	1.00	0.042	0.047	0.089	0.095	+6.3
No. 3	1.00	0.020	0.047	0.067	0.066	−1.5

within the limits of experimental error of this method. Table 3 also shows the reproducibility of the method. Samples containing various amounts of iodine were analyzed in replicate by this method. The precision of this method was within 10% except for very low concentrations.

The Recovery of Known Amounts of Iodine. The method was also checked by adding known amounts of iodate to 1.0-g rock samples. The results, presented in Table 4, show the relative errors of the determination to be less than 6.6%. According to these results, it may be concluded that the loss of iodine during the fusion was insignificant and that no major source of interference was present in the rock samples analyzed.

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