The Determination of Sulfide- and Sulfate-Sulfur in Igneous Rocks with Tin(II)-Strong Phosphoric Acid and Strong Phosphoric Acid[1]

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A method for the determination of minute amounts of sulfide- and sulfate-sulfur in igneous rocks was investigated. A rock sample is easily dissolved by heating with tin(II)-strong phosphoric acid or strong phosphoric acid. When the rock sample is dissolved with tin(II)-strong phosphoric acid, total-sulfur is evolved as hydrogen sulfide. With strong phosphoric acid, sulfide-sulfur is evolved as hydrogen sulfide, but sulfate-sulfur is not. The hydrogen sufide evolved is fixed as zinc sulfide, and then determined by the photometric method, using mercuric thiocyanate and ferric iron. The conditions for separating sulfide- and sulfate-sulfur in rocks were examined by using samples which had been prepared by mixing rock or silica (each of them, $<0.001\%$ S) with sulfides or sulfates. The application of the method to some igneous rock samples gave results with a coefficient of variation of about 5% for sulfur contents of 0.01—0.02%. The sulfur in samples with more than 0.001% can be determined by using about 0.1 g of samples. The sulfide- and sulfate-sulfur in two standard rock samples were also determined: W-1 (Total-S, 0.012%; Sulfide-S, 0.005%; Sulfate-S, 0.007%) and G-1 (Total-S, 0.004%, Sulfide-S, $<0.001\%$; Sulfate-S, 0.004%).

It has been said that sulfur in igneous rocks exists in the forms of sulfides and sulfates. The proportion of sulfide- and sulfate-sulfur, and their amounts, would reflect the conditions of igneous rocks at the time of formation. In 1960, Ricke[2] determined the sulfide- and sulfate-sulfur content of rocks by two titrimetric methods. Recently, Schneider[3] separated the sulfide- and sulfate-sulfur in basalts, and measured the isotope composition of each sulfur. However, their methods have some defects. In these methods, rock sample is treated with hydrochloric acid in the separation of sulfide- and sulfate-sulfur. The decomposition of rocks, however, requires a very long time (more than about 6 hr). Moreover, the rock sample is not perfectly dissolved with hydrochloric acid, and all the sulfide-sulfur in the sample may not be determined. Moreover, they did not check that sulfate-sulfur was not determined in the determination of sulfide-sulfur.

One of the present authors (T. O.) and others[4] have previously reported a sensitive method for the determination of total-sulfur in igneous rocks. The method consists of decomposing a rock sample by heating it with tin(II)-strong phosphoric acid,[5] releasing the sulfur as hydrogen sulfide, and finally determining it by the photometric method, using mercuric thiocyanate and ferric iron.[6] A rock sample is easily dissolved with tin(II)-strong phosphoric acid or strong phosphoric acid. The present authors were aware that when the sample is dissolved with strong phosphoric acid without tin(II), sulfide-sulfur is evolved as hydrogen sulfide, while sulfate-sulfur is not.

It is not clearly known what forms of sulfur exist in usual igneous rocks, for the sulfur content is generally very low. However, many investigators[7-10] have microscopically detected sulfides in igneous rocks with relatively high contents of sulfur, *e.g.* pyrite, pyrrhotite, chalcopyrite, pentlandite, bornite, cubanite, covellite, and digenite. Schneider[3] forecast the sulfate-sulfur in basalts as follows: (a) as sulfate minerals, *e.g.* barite, anhydrite, nosean, and haüyne; (b) in the crystal lattice of silicates and apatite; (c) in fluid inclusions.

On the other hand, we expected pyrite, pyrrhotite, chalcopyrite, barium sulfate and calcium sulfate as typical sulfur compounds in igneous rocks. In order to examine the conditions for separating sulfide- and sulfate-sulfur, samples were prepared by mixing rock or silica with these sulfides or sulfates.

Experimental

Apparatus. The apparatus used in this study (Fig. 1 and 2) was mostly the same as that described by Arikawa *et al.*[4]

The nitrogen flow rate was measured by a Kusano flowmeter KG-1 type.

A Hirama photoelectric-spectrophotometer type 6, and 10 mm cells were used to measure the absorbance.

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

Strong Phosphoric Acid: This reagent was prepared by heating 1000 g of orthophosphoric acid (d=1.7) in a round bottomed silica flask (Fig. 1) up to 250°C on a mantle heater.

Tin(II)-Strong Phosphoric Acid: This reagent was prepared by heating 78 g of stannous chloride dihydrate and the above obtained strong phosphoric acid in the round-bottomed silica flask up to 280°C on the mantle heater.

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[1] A part of this report was presented at the 20th Annual Meeting of the Japan Society for Analytical Chemistry, Tokyo, Oct., 1971.

[2] W. Ricke, *Geochim. Cosmochim. Acta*, **21**, 35 (1960).

[3] A. Schneider, *Contr. Mineral. Petrol.*, **25**, 95 (1970).

[4] Y. Arikawa, T. Ozawa, and I. Iwasaki, *Bunseki Kagaku*, **21**, 920 (1972).

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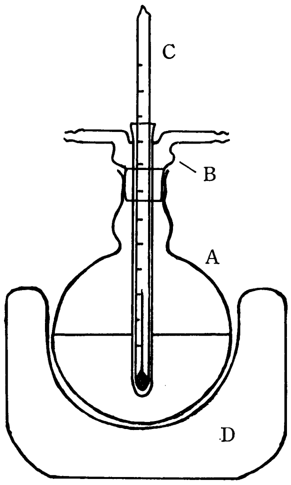

Fig. 1. Apparatus for the preparation of strong phosphoric acid and tin(II)-strong phosphoric acid.
A: Round-bottomed silica flask (1 *l*), B: Gas-delivery silica cap with thermometer-protecting tube, C: Thermometer (360°C), D: Mantle heater.

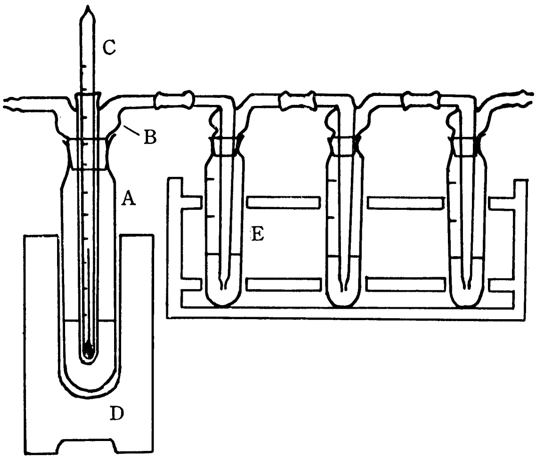

Fig. 2. Apparatus for the determination of total- and sulfide-sulfur.
A: Silica test tube (inner-diameter: 3.5 cm, length: 17 cm), B: The same as B in Fig. 1, C: Thermometer (360°C), D: Electric furnace, E: Absorption tube: centrifuge tube (15 m*l*) fitted with gas-delivery cap.

Standard Sodium Sulfate: Dissolve 4.43 g of dried sodium sulfate in water and dilute to exactly 1 *l*. The solution is standardized by the gravimetric method of the determination of sulfate as barium sulfate. It contains 1 mg of sulfur per m*l*. Prepare the working solution by diluting this solution adequately.

Saturated Barium Hydroxide Solution:

Zink Sulfate Solution (3%): Dissolve 5.3 g of zinc sulfate heptahydrate in water and dilute to 100 m*l*.

*Sodium Hydroxide Solution (1*M*)*:

*Acetic Acid Solution (1*M*)*:

Mercuric Thiocyanate Solution: Solid mercuric thiocyanate was prepared as has been described by Utsumi.[11] Dissolve 0.5 g of mercuric thiocyanate in 100 m*l* of methyl alcohol.

Ferric Nitrate-Perchloric Acid Solution: Dissolve 28.3 g of ferric nitrate in 100 m*l* of a 4M perchloric acid solution.

Sodium Carbonate Solution (1%):

Carbon Tetrachloride: *Nitrogen Gas*: Nitrogen from a commercial cylinder is purified with an alkaline pyrogallol solution, and then dried with solid calcium chloride.

Preparation of Mixed Samples. The mixed samples (Table 1) were prepared by the following procedure. For example, in the case of mixing rock with pyrite, 1 g of a finely-powdered rock and 0.03 g of pyrite were thoroughly mixed in an agate mortar with a pestle for one hour. They were mixed again with 2 m*l* of carbon tetrachloride for one hour. Next, 0.1 g of the mixed sample and 1 g of rock were mixed in the same manner. The procedure was repeated by using 0.1 g of this mixed sample and 1 g of rock. The other mixed samples were also prepared by the same procedure. These samples contained about 15 μg of sulfur per 100 mg. In the present study, basalt from Aokigahara, Mt. Fuji, Yamanashi Prefecture, silica (99.99%) from the Ko-Jundo-Kagaku Institute (their total-sulfur contents were less than 0.001%), pyrite from Udo Mine, Shimane Prefecture, pyrrhotite from Yanahara Mine, Okayama Prefecture, and chalcopyrite from Miyatamata Mine, Akita Prefecture, were used. The barium sulfate and the calcium sulfate were prepared from a barium chloride solution, a calcium chloride solution, and sulfuric acid.

Procedure and Calibration Curve. *Procedure (1) (the Determination of Total-Sulfur)*: In a silica test tube, place about 0.1 g of a finely-powdered rock sample and 15 m*l* of tin(II)-strong phosphoric acid. Mix them with a silica rod (length: about 18 cm). During the heating, keep this rod in the test tube. Into three absorption tubes, add 0.5 m*l* of a zinc sulfate solution (3%), 3 drops of a 1M sodium acetate solution, and about 4.5 m*l* of water respectively. Connect all the parts of the apparatus, as is shown in Fig. 2. Introducing nitrogen gas (flow rate, 50—180 m*l*/min), heat the silica test tube by an electric furnace (800W). When it reaches 280°C,[12] keep it at 280±3°C for 30 min by using a slide auto-transformer. Disconnect the absorption tubes from the apparatus, and rinse the inside of the first absorption tube's cap into the tube with a small quantity of water. To it add one drop of phenolphthalein as an indicator, and then 0.1M sodium hydroxide solution dropwise until the color changes. By this procedure, micro amounts of zinc sulfide coprecipitate with zinc hydroxide. After centrifugation, discard the supernatant liquid. Into the absorption tube, transfer the solution in the second absorption tube. Run the same procedure again, and then repeat it for the solution in the third absorption tube. In order to wash the precipitate, add 3 m*l* of a sodium carbonate solution (1%) and about 7 m*l* of water, shake vigorously, centrifuge, and discard the supernatant liquid. To the precipitate, add 0.5 m*l* of a 1M acetic acid solution, 1 m*l* of a mercuric thiocyanate solution, and 2 m*l* of a ferric nitrate-perchloric acid solution, in this order. After diluting to exactly 10 m*l* with water, in order to collect the mercuric sulfide, add 0.5 m*l* of carbon tetrachloride, shake vigorously, and centrifuge. Measure the absorbance of the supernatant liquid at 460 mμ, using water as the reference.

Procedure (2) (the Determination of Sulfide-Sulfur): Using the apparatus shown in Fig. 2, place about 0.1 g of a finely-powdered rock sample containing less than about 10 mg of ferrous iron as ferrous oxide and 15 m*l* of strong phosphoric acid. The subsequent procedure is the same as that described in (1).

Calibration Curve: The calibration curve (Fig. 3) was obtained by using a standard sodium sulfate solution (0—30 μg as S) and 2 drops of a saturated barium hydroxide solution,

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

[12] The time necessary to reach 280°C is about 20 min after the start of heating.

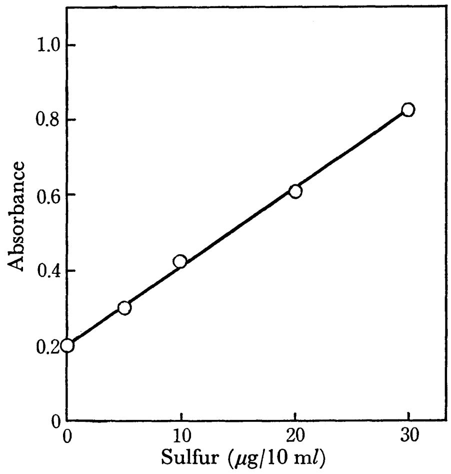

Fig. 3. Calibration curve.

which had been evaporated to dryness in a silica test tube; the sulfur was subsequently determined by Procedure (1).

Results and Discussion

The total-sulfur in igneous rocks was determined by the method of Arikawa *et al.*[4] With a slight modification of the method, several tests were carried out.

The Effect of the Heating Time on Procedure (1). The recovery of sulfur was examined by varying the heating time (5—40 min) using the standard sodium sulfate solution (30 μg as S). The heating time of 30 min was decided on the basis of the results (Fig. 4).

The Effect of the Nitrogen Flow Rate on Procedure (1). The recovery of sulfur was tested by varying the nitrogen flow rate (50—180 ml/min) using the standard sodium sulfate solution (30 μg as S). The results (Fig. 5) indicate that the nitrogen flow rate in this range has no effect on the recovery of sulfur.

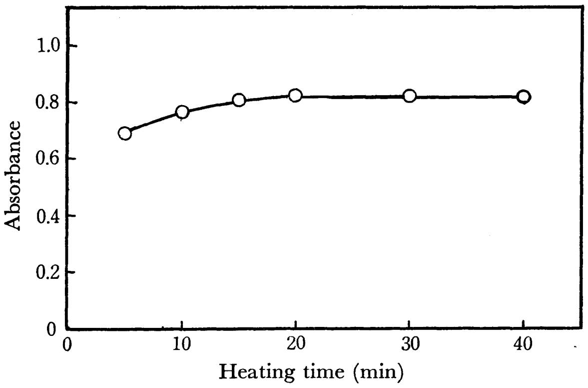

Fig. 4. Effect of the heating time on Procedure (1).

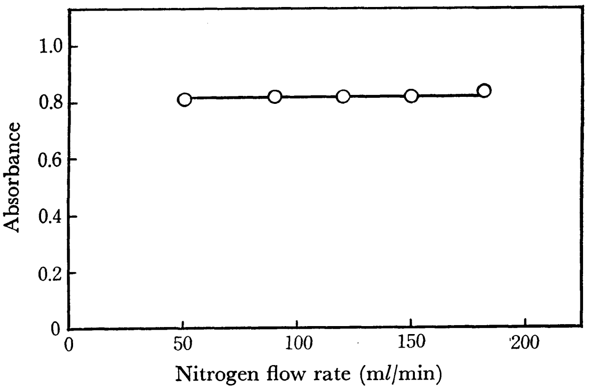

Fig. 5. Effect of the nitrogen flow rate on Procedure (1).

Table 1. Determination of total-sulfur in the mixed samples by procedure (1)

Sample	S (μg) added	S (μg) found	S (μg) difference	Relative deviation (%)
Rock+FeS_2	15.7	15.3	−0.4	2.5
	17.5	17.2	−0.3	1.7
	19.2	19.3	+0.1	0.5
Rock+FeS	17.6	17.6	0	0
	20.7	20.9	+0.2	1.0
Rock+$CuFeS_2$	17.3	17.1	−0.2	1.2
	20.0	20.0	0	0
SiO_2+FeS_2	10.2	9.8	−0.4	3.9
	24.3	25.0	+0.7	2.9
Rock+$BaSO_4$	19.7	18.9	−0.8	4.1
	21.4	22.1	+0.7	3.3
	26.9	27.2	+0.3	1.1
Rock+$CaSO_4$	9.7	10.0	+0.3	3.1
	19.4	19.0	−0.4	2.1
SiO_2+$BaSO_4$	14.5	14.1	−0.4	2.8
	29.0	29.5	+0.5	1.7

Rock: Basalt (Mt. Fuji, S: $\leqslant$0.001%)

Determination of Total- and Sulfide-Sulfur in Mixed Samples. The mixed samples previously described were analyzed by Procedure (1). As Table 1 shows, the results give values with a relative deviation of less than 5%. The total-sulfur in the forms of both sulfides and sulfates can be determined by Procedure (1). Therefore, if only the sulfide-sulfur in igneous rocks can be determined, the sulfate-sulfur content can be obtained from the difference between the total- and the sulfide-sulfur.

The condition of determining only the sulfide-sulfur with strong phosphoric acid was examined by using the mixed samples. At first, the mixed sample of rock-pyrite and that of rock-barium sulfate (each of them including about 15 μg of S) were used. The

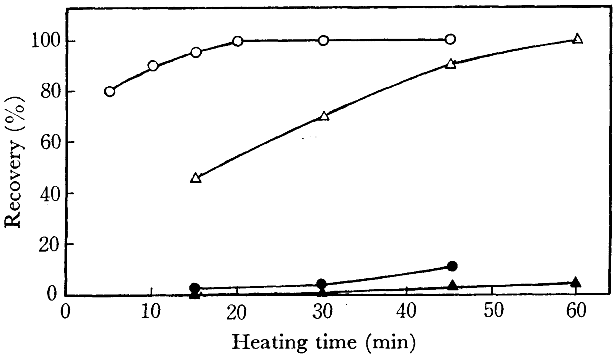

Fig. 6. Determination of sulfide-sulfur with strong phosphoric acid (1).

○ Rock+FeS_2 } at 280°C
● Rock+$BaSO_4$

△ Rock+FeS_2 } at 260°C
▲ Rock+$BaSO_4$

These samples contain about 15 μg as S.

temperature (260 and 280°C) and the heating time (5—60 min) were varied. The results are given in Fig. 6. At 280°C, the sulfur in the mixed sample of rock-pyrite is completely recovered in 30 min At the same temperature, the sulfur in the mixed sample of rock-barium sulfate is partly evolved as hydrogen sulfide. Within 30 min, the amount of sulfur is almost negligible ($<5\%$), but in 45 min it grows appreciable ($>10\%$). The sulfate-sulfur sppears to be reduced by the ferrous iron in the rock. This problem will be discussed later. At 260°C, the results of the heating time of 60 min seem to be the same as those of the heating time of 30 min at 280°C. However, the use of 260°C requires a longer time than does that of 280°C. Therefore, the heating time of 30 min at 280°C has been investigated further.

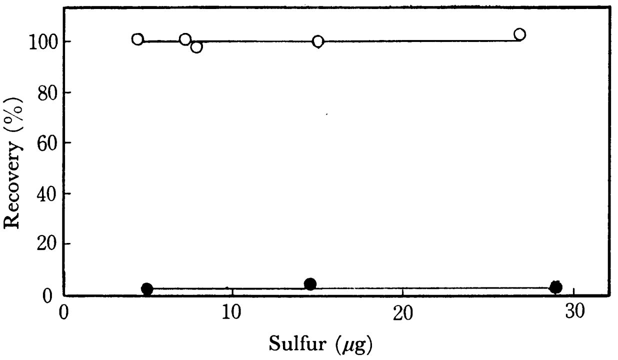

Fig. 7. Determination of sulfide-sulfur with strongs phosphoric acid (2).
○ Rock+FeS_2 } at 280°C
● Rock+$BaSO_4$ }
Heating time: 30 min

Under this conditions and using Procedure (2), recovery was tested using various amounts of the mixed sample of rock-pyrite and that of rock-barium sulfate. According to the results (Fig. 7), the sulfur in the mixed sample of rock-pyrite is completely recovered, and the evolution of sulfur in the mixed sample of rock-barium sulfate is almost negligible ($<5\%$).

The results of the recovery tests by means of Procedure (2) and using various kinds of mixed samples are summarized in Table 2. They indicate that the separation of the sulfide- and the sulfate-sulfur is possible.

TABLE 2. DETERMINATION OF SULFIDE-SULFUR IN THE MIXED SAMPLES BY PROCEDURE (2).

Sample	S added (μg) as sulfide	S added (μg) as sulfate	S found (μg)
Rock+FeS+$BaSO_4$	16.9	9.5	16.7
	23.0	19.3	22.0
Rock+FeS_2	14.9		15.0
	26.0		26.7
Rock+FeS	17.4		16.7
	23.0		22.0
Rock+$CuFeS_2$	17.5		18.0
	20.0		19.1
SiO_2+FeS_2	12.6		11.6
	30.0		29.3
Rock+$BaSO_4$		14.5	<1
		29.0	<1
Rock+$CaSO_4$		16.0	<1
		24.0	<1
SiO_2+$BaSO_4$		14.2	<1
		30.0	<1
Rock+FeS_2+$BaSO_4$	12.1	9.7	12.8
SiO_2+FeS_2+$BaSO_4$	18.9	14.5	17.8

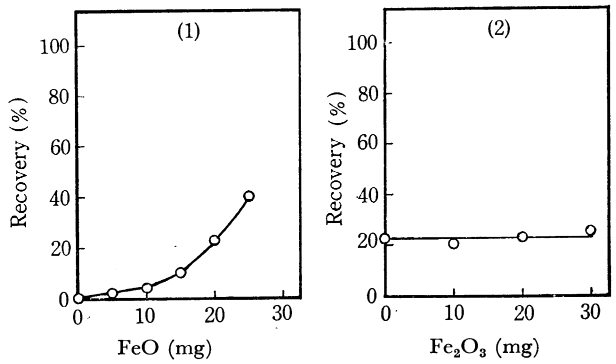

Fig. 8. Effect of iron on Procedure (2).
Procedure (2) was done by taking standard sodium sulfate solution (15 μg as S) and various amounts of iron oxide in the silica test tube.
(1) Fe_2O_3 not added (2) FeO: 20 mg

The Effect of Ferrous Iron on Procedure (2). As has already been mentioned, it has been thought that, in Procedure (2), the sulfate-sulfur is partly reduced by the ferrous iron in the rock. This point was checked by using the standard sodium sulfate solution (15 μg as S) and various amounts of iron oxide. As the ferrous oxide, wüstite (Found: FeO, 98%) was used; it had been synthesized as described by Darken and Gurry.[13] The ferric oxide was prepared from a ferric chloride solution and aqueous ammonia. The sulfur contents of these oxides were less than 0.001%. The results (Fig. 8) indicate that sulfate-sulfur is partly reduced in the presence of ferrous oxide. The evolution of sulfur is almost negligible ($<5\%$) with less than about 10 mg of ferrous oxide. It is independent of the amount of ferric oxide in the range of 0—30 mg. Therefore, in analysis by Procedure (2), a rock sample which contains less than about 10mg of ferrous iron as ferrous oxide should be placed in a silica test tube.

The Determination of Sulfide- and Sulfate-Sulfur in Rock Samples. In order to confirm the reproducibility of the method, various igneous rock samples were analyzed by Procedures (1) and (2). These results (Table 3) show the coefficient of variation to be about 5% for sulfur contents of 0.01—0.02%.

The method was also checked by adding known amounts of sulfide- and sulfate-sulfur to the sample No. 3. The results (Table 4) are in good agreement with the values in Table 3.

The Analysis of Standard Rocks. The sulfide- and sulfate-sulfur in two standard rock samples, G-1 and W-1, prepared by the U. S. Geological Survey, were also determined by Procedures (1) and (2) (Table 5). The data reported previously for the two rock samples

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[13] L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, **67**, 1398 (1945).

TABLE 3. DETERMINATION OF SULFUR IN IGNEOUS ROCKS

Sample No. 1: Andesite; Lave of 1946, Sakura-jima, Kagoshima Pref.

	Total-S				Sulfide-S			Sulfate-S
	Sample taken (g)	S found (μg)	S (%)		Sample taken (g)	S found (μg)	S (%)	S (%)
1	0.0563	10.0	0.018	1	0.0652	13.2	0.020	−0.002
2	0.1120	21.3	0.019	2	0.0875	17.0	0.019	0
3	0.1188	23.6	0.020	3	0.1028	18.5	0.018	0.002
4	0.1325	26.2	0.020	4	0.1243	23.6	0.019	0.001
5	0.1472	27.0	0.018	5	0.1446	26.7	0.018	0
			0.019_0	Mean			0.018_8	<0.001
			0.0010	Standard deviation			0.0008	—
			5.3	Coefficient of variation			4.3	—

Sample No. 2: Alkali rhyolite; Madara-jima, Saga Pref.

	Total-S				Sulfide-S			Sulfate-S
	Sample taken (g)	S found (μg)	S (%)		Sample taken (g)	S found (μg)	S (%)	S (%)
1	0.0546	5.0	0.009	1	0.0567	<1	<0.001	0.009
2	0.0887	8.7	0.010	2	0.0935	1.1	0.001	0.009
3	0.1048	10.5	0.010	3	0.1155	<1	<0.001	0.010
4	0.1243	12.1	0.010	4	0.1252	1.2	0.001	0.009
5	0.1514	14.7	0.010	5	0.1430	<1	<0.001	0.010
			0.009_8	Mean			<0.001	0.009_4
			0.0004	Standard deviation			—	0.0005
			4.1	Coefficient of variation			—	5.3

Sample No. 3: Trachyte; Nishino-shima, Oki, Shimane Pref.

	Total-S				Sulfide-S			Sulfate-S
	Sample taken (g)	S found (μg)	S (%)		Sample taken (g)	S found (μg)	S (%)	S (%)
1	0.0524	8.7	0.017	1	0.0473	3.5	0.007	0.010
2	0.0838	13.1	0.016	2	0.0810	5.1	0.006	0.010
3	0.1041	18.7	0.018	3	0.1022	6.2	0.006	0.012
4	0.1323	22.5	0.017	4	0.1221	8.4	0.007	0.010
5	0.1548	25.4	0.016	5	0.1511	12.2	0.008	0.008
			0.016_8	Mean			0.006_8	0.010_0
			0.0008	Standard deviation			0.0008	0.0014
			4.8	Coefficient of variation			11.8	14.0

TABLE 4. ADDITION TESTS

Total-S					Sulfide-S					Sulfate-S
Sample taken (g)	S (μg)			S (%)	Sample taken (g)	S (μg)			S (%)	S (%)
	added	found	added − found			added	found	added − found		
0.1034	6.8 (as FeS_2)	22.9	16.1	0.016	0.0973	6.1 (as FeS_2)	13.8	7.7	0.008	0.008
0.1047	5.6 (as FeS)	21.9	16.3	0.016	0.1044	6.0 (as FeS)	13.3	7.3	0.007	0.009
0.1009	9.7 (as $BaSO_4$)	26.5	16.8	0.017	0.0988	9.7 (as $BaSO_4$)	7.9	—	0.008	0.009

Sample: Sample No. 3.

(shown in Table 5) indicate a very wide scatter. According to the present analysis, for the total-sulfur our value of W-1 is in good agreement with the values of Ricke[2] and Frost *et al.*,[14] but our value of G-1 is lower than both of theirs, being nearer to the value of Frost *et al.* than to Ricke's. For the sulfide-sulfur, our values of W-1 and G-1 are significantly lower than those of Ricke.

TABLE 5. ANALYSIS OF STANDARD ROCKS

Sample	S (%)			
	Total-S	Sulfide-S	Sulfate-S	
W-1	0.012	0.005	0.007	a)
	0.0135	0.0130	0.0005	ref. 2)
	0.0124			ref. 14)
	0.0003			ref. 15)
G-1	0.004	<0.001	0.004	a)
	0.0175	0.0060	0.0115	ref. 2)
	0.0074			ref. 14)
	0.0003			ref. 15)

a) The present data.

Conclusion

By the use of the present method, the determination of sulfide- and sulfate-sulfur in igneous rocks is possible with tin(II)-strong phosphoric acid and strong phosphoric acid. The method is excellent in that a rock sample can be easily dissolved by heating for a relatively brief time (30 min), and the sulfide- and sulfate-sulfur in rocks can be determined by using the above two reagents respectively in the same procedure. The application of this method to some igneous rock samples gave results with a coefficient of variation of about 5% for sulfur contents of 0.01—0.02%. The sulfur in samples with more than 0.001% can be determined by using about 0.1 g of samples. The time necessary to analyze one sample is about two hours.

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14) I. C. Frost and J. A. Thomas, as Private communication (1964) quoted in *Geochim. Cosmochim. Acta*, **29**, 1263 (1965).

15) R. Brown and W. A. Wolstenholme, *Nature*, **201**, 598 (1964).