Rapid Determination of Inorganic Sulfur in Various Forms, Particularly in Sulfide Ores, by the Tin(II)-Strong Phosphoric Acid Reduction Method

By Toshiyasu KIBA, Ikuko AKAZA and Nobuyuki SUGISHITA

(Received August 12, 1957)

Previously it was shown that both soluble and insoluble sulfates could be easily reduced to hydrogen sulfide by heating with tin(II)-strong phosphoric acid, a new powerful and stable reducing agent first described by the authors[1]. The discovery of this reagent led the authors to the development of a new rapid and simple method for the determination of sulfate sulfur, in which hydrogen sulfide evolved by the reaction was absorbed by zinc acetate solution and titrated iodimetrically or estimated colorimetrically as usual. Both the volumetric procedure for semimicro scale and the colorimetric method for micro quantities of sulfate were already established by the authors and have been widely accepted in this country for investigative and industrial purposes[1,2]. Extension of this method to rapid determination of organic sulfur was also accomplished in this laboratory[3]. The organic sulfur was oxidized to sulfate by means of chromium(VI)-strong phosphoric acid and then estimated in the same way as inorganic sulfates, the volumetric or the colorimetric method being used in the final stage according to the sulfur content of the sample[4].

The present paper describes a later investigation in which the above method was extended to the determination of inorganic sulfur in other forms, e. g., thiosulfates, sulfites, thiocyanates and sulfides, in particular to rapid estimation of sulfur in sulfide ores such as pyrite, galena and zinc blende. The rapidity and the simplicity of the original method are retained in this procedure, in which all the sulfur in the samples is converted into hydrogen sulfide and determined iodimetrically.

Experimental

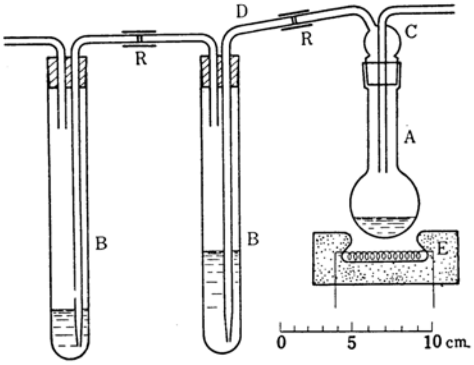

Fig. 1. Apparatus for reduction and absorption.
A: Reaction vessel, a round bottom flask
B: Absorbing vessels
C: Glass cap fitted to the reaction vessel
D: Gas-delivery tube
R: Short pieces of rubber tubing
E: Electric heater

Apparatus:—The apparatus used in this study is shown in Fig. 1. It is composed of two parts, a reaction vessel (A) and an absorption part (B). The reaction vessel (A) is a round bottomed flask of hard glass having a glass cap fitted to its top and provided with inlet and outlet tubes. The absorption part (B) is composed of two test-tubes 3 cm. in diameter. A gas delivery tube (D) is connected with a piece of rubber tubing to the outlet arm of the reaction vessel (A) and inserted into the absorbing solution. A Kipp's apparatus is employed for the production of carbon dioxide, which is purified by six gas-washing bottles (not shown Fig. 1.) and introduced into the reaction vessel through the inlet arm. The solutions used for the purification of carbon dioxide are described below.

Reagents:—*Storong Phosphoric Acid.*—Four hundred grams of commercial ortho phosphoric acid of extra pure grade (d=1.7) is placed in a 300-ml. flask or a 350 ml. conical beaker, and dehydrated by heating on a hot plate until a thermometer dipped in the liquid indicates 300°C. If the heating takes too long a time the liquid will become extremely turbid and viscous, and useless for the purpose in view. During the heating, the water vapor and the mist of phosphoric acid evolved should be rapidly removed from the neighborhood of the liquid surface through a glass tube, an end of which is hung down near the liquid surface, the other end being connected to a suction pump. It saves much time in heating.

---

1) T. Kiba et al., This Bulletin **28**, 641 (1955).
2) T. Kiba and I. Kishi, (present surname Akaza), ibid., **30**, 44 (1957).
3) S. Ohashi, ibid., **28**, 645 (1955).
4) T. Kiba, I. Akaza and S. Taki, ibid., **30**, 482 (1957).

Tin(II)-Strong Phosphoric Acid.—Fifty grams of tin(II)-chloride dihydrate of extra pure grade is placed in a 300-ml. conical beaker and on it, is poured 250 g. of the strong phosphoric acid prepared above. The content is heated within about one hour to 300°C after the manner of the preparation of the strong phosphoric acid. After cooling the tin(II)-strong phosphoric acid thus obtained, a very viscous and occasionally turbid liquid, may be stored in a closed vessel.

Zinc Acetate Solution, 4% or 8%.—Forty or 80 g. of zinc acetate dihydrate of pure grade is dissolved in 1 l. of distilled water. If necessary, two or three drops of glacial acetic acid are added to clarify the solution, but the pH of the solution should not fall below 5. A solution of suitable concentration is used depending upon the amount of sulfur to be analyzed.

Iodine, 0.02 N or 0.05 N.—These are standardized accurately by the ordinary procedure. Either of them is used depending on the amount of sulfur to be analyzed.

Sodium Thiosulfate, 0.02 N or 0.05 N.—These are standardized accurately by the ordinary procedure.

Carbon Dioxide.—Carbon dioxide produced in the Kipp's apparatus is purified by passing it through five gas-washing bottles containing, respectively, water, 1% potassium permanganate in 10% sodium carbonate solution, 2% vanadium(II) sulfate in 6N sulfuric acid solution[3], 5% barium chroride, and a zinc acetate absorbing solution. A sixth empty bottle is placed to intercept the droplets coming from the washing liquids.

Barium Hydroxide Solution.—Barium hydroxide dihydrate crystals of pure grade are saturated in distilled water and stored away from atomospheric carbon dioxide.

Bromine Water.—Bromine of pure grade is saturated in distilled water.

Various Samples Containing Sulfur.—Pure grade reagents of sodium thiosulfate, barium thiosulfate, sodium sulfite, potassium thiocyanate, and sodium sulfide were employed for the evaluation of the method. The salts were dissolved in water to prepare solutions of known concentration. The sulfur content of a definite volume of each solution was estimated by the conventional gravimetric or volumetric method. The sulfide ores used were natural pyrite, zinc blende and galena, from Ogoya Mine near Kanazawa city, and their sulfur contents were estimated by the gravimetric analysis according to the procedure described in ordinary text-books.

Procedure:—*Procedure A.*—Take an accurately measured sample—pipet a solution; weigh a solid—containing less than 20 mg. of sulfur and put it into the reaction vessel (A, Fig. 1). Add 0.5 ml. of the barium hydroxide solution, and evaporate the content to dryness at the bottom of the vessel. Pour 10 ml. of tin(II)-strong phosphoric acid over the dried residue with a pipet. Put 40 ml. of the zinc acetate solution into the first absorbing vessel and 20 ml. of the same solution into the second. Connect all the apparatus as shown in Fig. 1. Pass carbon dioxide very rapidly through the apparatus for five minutes to expel the air from the apparatus. Then reduce the flow of the gas to a rate of one bubble per second. Heat the bottom of the reaction vessel on a small electric heater which is regulated by a variable transformer, until white fumes of the strong phosphoric acid appear. It is unnecessary to keep the reaction temperature constant, but it should be high enough to ensure that the content of the vessel exhibits a white turbidity near the end of the reaction. Stop the heating and continue the passage of carbon dioxide for five minutes.

Disconnect the absorbing vessels from the gas-outlet arm of the reaction vessel and quickly pour into them 20 ml. of 0.02 N iodine solution—the bulk into the first vessel and only a bit into the second. A part of the zinc sulfide precipitate may cling to the glass tubes; it is allowed to remain in the absorbing vessels. Swirl the vessel to mix the content thoroughly, transfer it to a beaker and back titrate the excess of the iodine with 0.02 N sodium thiosulfate solution using starch as indicator.

The whole determination can be carried out in thirty or forty minutes. A blank test should be run without a sample. One ml. of 0.02 N iodine corresponds to 0.3206 mg. of sulfur.

Procedure B.—Take the sample into the reaction vessel. Add two or three drops of the bromine water to oxidize the sulfur to sulfate form and then fix it as barium sulfate by adding 0.5 ml. of the barium hydroxide solution. Evaporate the content on a water-bath, and carry out the reduction of the sulfate according to Procedure A as shown above.

Thiosulfates, thiocyanates and sulfites should be treated by procedure B before the reduction with tin(II)-strong phosphoric acid.

Results and Discussion

Sulfide Ores.—Zinc blende, galena and pyrite were analyzed using procedure A. In Table I the results obtained by the gravimetric method are tabulated together. As all the sulfur in these sulfide ores could be generated as hydrogen sulfide by the simple treatment with the tin(II)-strong phosphoric acid, all troublesome treatments such as dissolving of the ores in acids and evaporation of the solution were dispensed with, in the course of the analysis. The determination of the sulfur could be accomplished very quickly—within twenty or thirty minutes. Because of the relatively small amount of the sample employed in this method care should be taken to grind the ore into fine powder and to mix it thoroughly, so that the sample may correctly represent the whole. The standard deviation (σ) and the average deviation (δ) of the results obtained by this method were comparable to those

TABLE I

DETERMINATION OF SULFUR IN SULFIDE ORES

A: Zinc Blende

Sample Taken[a)] mg.	S Found mg.	S Content[b)] %
37.46	11.84	31.60
37.47	11.63	31.03
40.33	12.64	31.34
42.65	13.18	30.90
47.69	15.03	31.49

($\sigma=0.246\%$, $\delta=0.298\%$)

a) The sample ore was ground into 200-mesh and weighed by a micro-balance.

b) The mean value of sulfur content obtained by gravimetric method was 30.12%.

B: Galena

By Procedure A			By Gravimetric Method	
Sample Taken[c)] mg.	S Found mg.	S %	Sample Taken g.	S Found %
73.52	9.38	12.75	0.2626	12.32
76.56	9.85	12.86	0.2900	12.79
82.53	10.48	12.69	0.2820	13.02
83.92	10.72	12.77	0.2685	12.09
96.19	12.13	12.61	0.3477	12.47
($\sigma=0.068\%$, $\delta=0.093\%$)			($\sigma=0.294\%$, $\delta=0.370\%$)	

c) The sample ore was ground into 200-mesh and weighed by a micro-balance.

C: Pyrite

By Procedure A			By Gravimetric Method (According to Lunge)	
Sample Taken[d)] mg.	S Found mg.	S %	Sample Taken g.	S Found %
16.50	8.61	52.18	0.0838	51.88
17.82	9.12	51.17	0.1107	51.04
26.63	13.90	52.19	0.1490	52.10
27.43	14.13	51.51	0.1252	52.14
28.51	14.61	51.24	0.1402	50.98
($\sigma=0.422\%$, $\delta=0.497\%$)			($\sigma=0.488\%$, $\delta=0.572\%$)	

d) The sample ore was ground into 200-mesh and weighed by a micro-balance.

by the gravimetric analysis. In both cases the ores were ground to about 200 meshes (per inch). Slightly higher values of sulfur content were obtained by this than by the gravimetric method. Probably because no sulfur in the sample was lost during the couse of this method, while with the gravimetric method, a small amount of the sulfur might escape as sulfur dioxide or hydrogen sulfide during the process of dissolution in acid and evaporation of the solution. The results obtained by this method may thus be regarded as more reliable.

Sulfide.—An aliquot of freshly prepared sodium sulfide solution was employed for the analysis, the sulfur content having been estimated by iodimetry. Two methods were employed here. In one of them procedure B was employed, and in the other a few drops of the zinc acetate solution were added to the sample and the sulfur was analysed by procedure A. The results obtained by the above two methods are shown in Table II, from which it is revealed that whether the oxidation of sulfide ion takes place or not, all of the sulfur in the sample is ultimately converted in to hydrogen sulfide by this reduction method.

TABLE II

DETERMINATION OF SULFUR IN SODIUM SULFIDE

S Contained in an Aliquot[a)] mg.	S Found By This Method mg.	Note
2.99	2.98	Zinc acetate was added.
〃	2.99	〃
〃	2.94	〃
〃	2.93	〃
〃	2.99	By procedure B.
〃	3.01	〃
〃	3.00	〃

a) The amount of the sulfide ion in an aliquot was determined by iodimetry.

TABLE III

DETERMINATION OF SULFUR IN THIOSULFATES

A: Barium thiosulfate $BaS_2O_3 \cdot H_2O$ (Purity of the sample: 99.95%) S content: 23.96%, analysis was carried out by procedure A.

Sample Taken mg. (A)	S Content (Calcd.) ($A \times 0.2396$) mg.	S Found mg.	S Found %
10.06	2.41	2.40	23.85
22.63	5.42	4.88	21.56
24.35	5.83	5.42	22.25
10.06	2.41	2.41	23.95
〃	〃	2.41	23.95
〃	〃	2.39	23.75
〃	〃	2.42	24.05
〃	〃	2.40	23.85
17.24	4.13	4.15	24.07
17.25	4.13	4.16	24.11
19.46	4.66	4.65	23.89

B: Sodium Thiosulfate $Na_2S_2O_3 \cdot 5H_2O$ (S content: 25.84%)

Sample Taken mg. (A)	S Content (Calcd.) ($A \times 0.2584$) mg.	S Found mg.	S Found %
17.16	4.43	4.44	25.87
〃	〃	4.42	25.75
〃	〃	4.43	25.81
8.58	2.21	2.22	25.87
〃	〃	2.22	25.87

Thiosulfate.—Sodium thiosulfate solution and barium thiosulfate solid were analyzed by procedure B. The thiosulfate ion could not be reduced quantitatively to hydrogen sulfide merely by heating with the tin(II)-stong phosphoric acid. It had to be oxidized to sulfate before the reduction. Assay of the sulfur in the sample was carried out by iodimetry. The results obtained are shown in Table III.

Sulfite.—An aliquot of sodium sulfite solution was employed for the analysis. The solution usually contains both sulfite and sulfate ions, for the former is easily oxidized to the latter during the preparation and storage of the solution; the content of the total sulfur, however, remains unaffected. The analysis was carried out according to procedure A and B, but the results coincide closely with each other as shown in Table IV.

TABLE IV

DETERMINATION OF SULFUR IN SODIUM SULFITE

Sample Taken mg. (A)	S Content (Calcd.) ($A\times0.2059$) mg.	S Found mg.	%	Procedure
20.14	4.15	4.14	20.55	A.
〃	〃	4.16	20.65	〃
〃	〃	4.14	20.55	〃
〃	〃	4.21	20.90	B.
〃	〃	4.13	20.50	〃
〃	〃	4.21	20.90	〃

a) Purity of the reagent as a solid: Na_2SO_3 60.225%

b) Total sulfur content of an aliquot taken was gravimetrically determined as barium sulfate; sulfur content: 20.59%.

TABLE V

DETERMINATION OF SULFUR IN POTASSIUM THIOCYANATE

Sample Taken ml. (A)	S Content (Calcd.) ($A\times3.84$ mg.)	S Found mg.	%	Procedure
2.0	7.68	2.56	11.04	A.
5.0	19.20	4.19	0.72	〃
2.0	7.68	7.64	32.83	B.
〃	〃	7.65	32.87	〃
〃	〃	7.74	33.26	〃
〃	〃	7.69	33.04	〃
3.0	11.52	11.38	32.60	〃
〃	〃	11.58	33.18	〃
〃	〃	11.50	32.95	〃

a) Sulfur content of potassium thiocyanate was calculated from the results obtained by argentiometry. One milliliter of the solution used here contained 3.84 mg. of sulfur.

Thiocyanate.—A solution of potassium thiocyanate was used for the analysis. As sulfur in a thiocyanate can not be reduced to hydrogen sulfide merely by treatment with the tin(II)-strong phosphoric acid, procedure B was adopted for this compound. Results obtained by procedures A and B are listed together in Table V.

The determination of inorganic sulfur in various forms can be done by procedure A or by procedure B within thirty minutes. With reference to rapidity of analysis this method is greatly superior to all the conventional ones. In accuracy this method is comparable to gravimetric methods, but the amount of sample to be taken for analysis is far smaller than that needed for other routine methods, as shown in Table I in the case of sulfide ores.

Summary

The procedure for the determination of sulfate sulfur using a new reagent, tin (II)-strong phosphoric acid, previously devised by the authors, has been extended to the determination of sulfur in other forms of inorganic compounds, e.g., sulfide ores (zinc blende, galena and pyrite), sulfides, thiosulfates, sulfites and thiocyanates. Two procedures of the analysis have been proposed by the authors: one, suitable for sulfide ores, sulfides, and sulfites, in which samples are treated directly with tin(II)-strong phosphoric acid to reduce the sulfur to hydrogen sulfide, and the other, suitable for sulfites, thiosulfates, and thiocyanates, in which samples are previously treated with bromine water to oxidize the sulfur to sulfate, and the sulfate is reduced to hydrogen sulfide. The hydrogen sulfide evolved from the sample is absorbed in zinc acetate solution and titrated iodimetrically as usual. The rapidity and the simplicity of the original method are still retained in this case, by which less than 30 milligrams of sulfur in the sample can be estimated within thirty minutes with good reproducibility.

The expense of the present research was met in part by a Grant for Scientific Research from the Ministry of Education to which the authors' thanks are due.

Department of Chemistry, Faculty of
Science, Kanazawa University
Kanazawa