Rapid Determination of Sulfur in Organic Compounds by the Tin(II)-Strong Phosphoric Acid Reduction Method

By Shigeru OHASHI

(Received July 22, 1955)

Sulfur in organic compounds is usually determined by the Pregl, the Carius, or the fusion method. In all these methods sulfur in organic compounds is oxidized to sulfate by the dry or wet combustion method and then commonly estimated gravimetrically as barium sulfate. In other cases for the determination of sulfate formed by combustion, various volumetric or colorimetric methods have been described. Since all these methods are composed of two step procedures, i.e. the decomposition of samples and the estimation of sulfate, they require patient time and skilful technique. Recently the new methods based on a reduction with metallic potassium¹⁾ or lithium²⁾ have been reported on the determination of organic sulfur, but they are not yet generally accepted.

In this laboratory for the last four years strong phosphoric acid has been used as a very excellent reaction medium for many analytical purposes, and the new methods for the determination of elementary carbon³⁾, oxidation value of organic compounds⁴⁾, and nitrogen in organic compounds⁵,⁶⁾ using a strong oxidizing action of iodic acid in this medium have been already investigated. Recently in this laboratory it was also found that tin(II)-strong phosphoric acid has such a strong reducing action that sulfates can be quantitatively reduced to hydrogen sulfide by heating with it. By means of this reaction, sulfates can be very rapidly and simply determined volumetrically⁷⁾.

The present study has been carried out with the purpose of establishing a new rapid method for the determination of sulfur in organic compounds by means of this new reducing agent, tin(II)-strong phosphoric acid.

In this method sulfur in organic compounds is reduced to hydrogen sulfide by heating with the tin(II)-strong phosphoric acid reagent in the stream of carbon dioxide, and absorbed into zinc acetate solution. After the above reaction, by adding the definite amount of iodine solution into the absorbent solution and titrating the excess iodine with a standard solution of sodium thiosulfate, the sulfur is volumetrically determined. The procedure mentioned above in outline is for convenience called "Procedure A".

Since the sulfur contained in the compounds such as methylorange or cystine is easily reducible, it can be readily determined by the Procedure A. But the sulfur in the compounds such as thiourea or methionine can not be directly reduced by tin(II)-strong phosphoric acid. In such a case, after oxidizing the combined sulfur to sulfate or sulfonate by heating with chromium(VI)-strong phosphoric acid, the sulfur should be reduced to hydrogen sulfide by treating with tin(II)-strong phosphoric acid. This procedure is called "Procedure B". Chromium(VI)-strong phosphoric acid is also a new strong oxidizing agent which has been found in the author's laboratory.

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 vessel B. The vessel A is closed at the top by means of a rubber stopper R, through which a gas-introducing tube and a thermometer-protecting tube are inserted. Both tubes are connected with a rubber tube T. In the middle of the vessel A, there is a constricted part above which a small glass lock is set to protect it against the backstream of gas. As at high temperature strong phosphoric acid has a strikingly corrosive action against glass, the bottom glass of the vessel A, after being used many times, will become thin and be broken at last. Therefore, when it becomes thin to a certain extent, it should be thicken by heating with a gas burner.

The absorption vessel B is composed of three 100 ml. Erlenmeyer flasks which are connected to each other with glass tubes and rubber tubes. The first flask is a guard one and the second and third are absorption flasks.

Reagents

Strong Phosphoric Acid.—Extra pure grade 89% orthophosphoric acid was dehydrated by heating until the temperature of the liquid reaches 300°C.

---

1) W. Zimmermann, *Microchemie ver. Microchim. Acta*, **40**, 162 (1952).

2) M. Vecera, *Chem. Listy*, **48**, 613 (1954).

3) T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Japan Analyst*, **2**, 446 (1953).

4) S. Ohashi, This Bulletin, **28**, 171 (1955).

5) S. Ohashi, ibid., **28**, 177 (1955).

6) S. Ohashi, ibid., **28**, 537 (1955).

7) T. Kiba, T. Takagi, Y. Yoshimura and I. Kishi, ibid., **28**, 641 (1955).

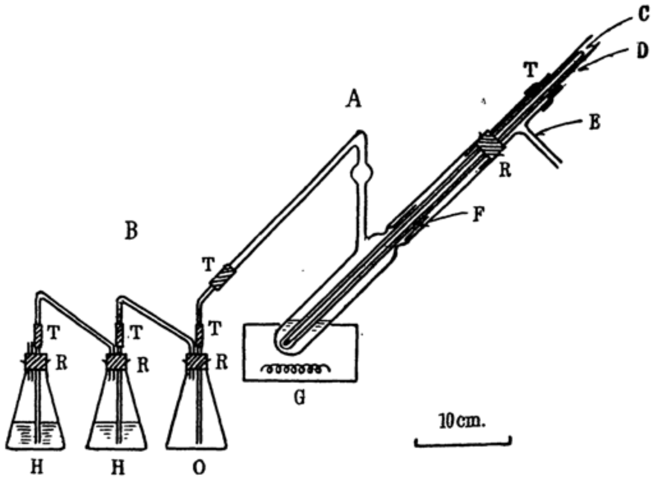

Fig. 1. Apparatus

A: Reaction Vessel
B: Absorption Vessel
C: Thermometer
D: Thermometer-Protecting Tube
E: Gas-Introducing Tube
F: Glass Lock
G: Electric Heater
H: Absorption Flasks
R: Rubber Stoppers
T: Rubber Tubes
O: Guard Flask

Its specific gravity was about 1.93[8].

Tin(II)-Strong Phosphoric Acid.—In a flask 20 g. of extra pure grade tin(II) chloride dihydrate was dissolved in 200 g. of strong phosphoric acid prepared as mentioned above and the mixture was heated at 300°C in the stream of carbon dioxide. By means of this treatment not only hydrogen chloride in the mixture was expelled, but also the trace of sulfur contained in tin(II) chloride was removed. The tin(II)-strong phosphoric acid thus prepared was stocked in a 100 ml. buret, which had an anhydrous calcium chloride-filled guard tube at the upper end, because strong phosphoric acid is very hygroscopic.

Chromium(VI)-Strong Phosphoric Acid.—In a beaker 15 g. of extra pure grade potassium dichromate was dissolved in 200 g. of strong phosphoric acid by heating on a water bath. This reagent was also stocked in the same manner as in the case of the tin(II)-strong phosphoric acid reagent.

Zinc Acetate Solution.—In about 200 ml. of water 40 g. of zinc acetate dihydrate and 30 ml. of glacial acetic acid were dissolved and the solution was diluted to 1 liter.

Iodine Solution.—About 0.02 N iodine solution prepared from iodine and potassium iodide was standardized against a 0.02 N standard solution of sodium arsenite.

Sodium Thiosulfate Solution.—About 0.02 N sodium thiosulfate solution was standardized against the above-mentioned 0.02 N iodine solution.

Carbon Dioxide.—Carbon dioxide was prepared from calcium carbonate and hydrochloric acid in a Kipp's apparatus and used after washing with potassium permanganate solution and the zinc acetate absorbent solution described above.

Procedure

Procedure A.—Weigh accurately a 10 to 30 mg. sample, depending upon its sulfur content, into a small weighing tube; choose the sample weight so that the liberated hydrogen sulfide will consume a half of the 0.02 N iodine solution, which will be used thereafter. Place the sample at the bottom of the reaction vessel and 7 ml. of tin(II)-strong phosphoric acid in it from the stock buret. Add each 20 ml. of the absorbent solution in both absorption flasks. Connect each part of the apparatus, expel the air in the reaction and absorption vessel by letting carbon dioxide flow, and heat the reaction medium at 250°-300°C for twenty minutes by means of a small electric heater. The hydrogen sulfide liberated from the medium is absorbed into the absorbent solution by sweeping with carbon dioxide and forms the white precipitate of zinc sulfide. After absorbing all of the liberated hydrogen sulfide, detach the absorption vessel from the reaction vessel and add 20 ml., the total amount, of the 0.02 N iodine solution in both absorption flasks at a suitable ratio. Usually the last flask does not contain zinc sulfide.

From a buret add the 0.02 N sodium thiosulfate solution to both absorption flasks until the greater part of the yellow color of iodine disappears. Transfer the solution in the flasks to a 300 ml. conical beaker, wash the flasks and the gas-conducting glass tubes with water, and titrate the excess iodine with the sodium thiosulfate solution in the presence of starch as indicator. If t_1 ml. is the volume of 0.02 N iodine solution used and t_2 ml. the volume of 0.02 N sodium thiosulfate, then,

---

[8] S. Ohashi, ibid., 28, 537 (1955).

$S\% = (t_1 - t_2)32.066/\text{sample weight (mg.)}$.

Procedure B.—Place a sample at the bottom of the reaction vessel, add 4 ml. of chromium(VI)-strong phosphoric acid in it from the stock buret, and warm the contents of the vessel on a water bath for about ten minutes. Next, gently heat the vessel on the electric heater for a few minutes. By this treatment all of the excess chromium(VI) compound, which will consume, if remains, the tin(II)-strong phosphoric acid, is decomposed to the green chromium(III) one. This chemical property of chromium(VI)-strong phosphoric acid is very interesting and advantageous for the present purpose. After the addition of tin(II)-strong phosphoric acid to the mixture in the reaction vessel, treat it subsequently in the same manner as in the Procedure A.

Results and Discussion

Analyses of some known organic compounds containing sulfur were carried out by this method. The results obtained by using the Procedure A are listed in Table I. It shows that sulfonic acid (methylorange), amide of sulfonic acid (sulfur guanidine), and an easily reducible sulfur such as that of cystine can be determined by the direct reduction method with tin(II)-strong phosphoric acid.

Table I

Determination of sulfur in organic compounds by the procedure A

Substance	Sulfur Content,	Sample Weight,	Sulfur Content	
			Found,	Deviation,
	%	mg.	%	%
Sulfur guanidine	14.97	22.7	15.0	0.0
$NH_2C_6H_4SO_2NHC(NH)NH_2$		〃	15.4	+0.4
		〃	15.3	+0.3
		〃	15.3	+0.3
		〃	14.9	−0.1
		〃	15.3	+0.3
		〃	15.1	+0.1
Methylorange	9.80	29.4	9.7	−0.1
$NaO_3SC_6H_4NNC_6H_4N(CH_3)_2$		30.0	9.6	−0.2
		30.5	10.0	+0.2
		22.2	10.3	+0.5
Cystine	26.69	12.3	25.2	−1.5
$(HOOCCH(NH_2)CH_2S\text{-})_2$		〃	25.8	−0.9
		〃	26.4	−0.3
		〃	26.5	−0.2
		〃	25.2	−1.5

Table II

Determination of sulfur in organic compounds by the procedure B

Substance	Sulfur Content,	Sample Weight,	Sulfur Content	
			Found,	Deviation,
	%	mg.	%	%
Methionine	21.49	14.1	22.2	+0.7
$CH_3SCH_2CH_2CH(NH_2)COOH$		〃	21.9	+0.4
		〃	22.3	+0.8
		〃	21.7	+0.2
		〃	21.8	+0.3
		〃	22.2	+0.7
		〃	9.0[a]	—
		〃	6.4[b]	—
Thiourea	42.12	10.9	41.0	−1.1
$CS(NH_2)_2$		9.3	42.2	+0.1
		27.5	40.7	−1.4
		10.5	41.5	−0.6
		7.3	20.4[c]	—
		7.3	11.3[c]	—
Acetylmethionine	16.77	15.6	17.1	+0.3
$CH_3SCH_2CH_2CH(NHCOCH_3)COOH$		14.0	17.0	+0.2
		16.2	16.6	−0.2
		20.5	16.3	−0.5
		11.4	16.9	+0.1

TABLE II (Contd.)

Substance	Sulfur Content, %	Sample Weight, mg.	Sulfur Content Found, %	Sulfur Content Deviation, %
Thionalide $C_{10}H_7NHCOCH_2SH$	14.76	16.7	15.1	+0.3
		14.4	15.5	+0.7
		20.2	14.9	+0.1
		16.0	14.5	−0.3
		19.7	14.4	−0.4
		15.4	14.3	−0.5
		16.8	14.6	−0.2
		23.1	13.1[c]	−1.7
		15.4	13.6[c]	−1.2

a) Oxidation with hydrogen peroxide.
b) Oxidation with a mixture of potassium permanganate and strong phosphoric acid.
c) Determination by the Procedure A.

The results of analyses carried out by the Procedure B are shown in Table II. Sulfur in methionine, thiourea, acetylmethionine, and thionalide can be determined by the oxidation with chromium(VI)-strong phosphoric acid followed by the reduction with tin(II)-strong phosphoric acid. The results obtained for methionine by using some oxidizing agents besides chromium(VI)-strong phosphoric acid and for thiourea by the direct reduction method (Procedure A) give all extremely low values as shown in Table II. For thionalide the Procedure A gives nearly correct values, but the Procedure B is more suitable.

For the analyses of sulfur guanidine, cystine, and methionine, dissolving the definite amounts of the samples in water or diluted hydrochloric acid, the aliquots of the obtained solution were evaporated in the reaction vessel and treated by the previously described procedure.

The determination of sulfur can be done by the Procedure A or B for thirty or forty minutes, respectively. With reference to rapidity of analysis this method is much more excellent than the various old ones. Accuracy of this method is not yet satisfactory, but it is useful enough for a routine analysis. The main source of the error may be probably due to the traces of sulfur contained in the reagents and apparatus used and of hydrogen sulfide remaining in the reaction medium.

The investigation on the chemical composition of tin(II)-strong phosphoric acid has been carried out in this laboratory[9] and led to the conclusion that the reducing power of this reagent is practically based on tin(II) ion. It was also found that this reagent, if protected from the moisture in the air, can be stored for one month without any change of its composition.

Chromium(VI)-strong phosphoric acid is decomposed rapidly and completely, if heated at about 170°C, but it is not decomposed practically, at least for one month, at room temperature. This fact is shown in Table III. In this experiment, in order to determine the content of Cr(VI) in chromium(VI)-strong phosphoric acid, potassium iodide was added to the solution, which was obtained by dissolving the definite amount of chromium(VI)-strong phosphoric acid in water, and the liberated iodine was titrated with 0.1 N sodium thiosulfate solution.

TABLE III
STABILITY OF CHROMIUM(VI)-STRONG PHOSPHORIC ACID AT A ROOM TEMPERATURE

Date	Sample Weight, g.	0.1 N $Na_2S_2O_3$, ml.	$K_2Cr_2O_7$, %
Nov. 22	1.233	11.35	4.53
〃	1.679	15.49	4.54
Nov. 29	1.803	16.46	4.47
〃	1.714	15.76	4.50
Dec. 4	2.545	23.14	4.46
〃	2.306	20.92	4.45
Dec. 13	1.771	16.00	4.43
〃	1.652	14.85	4.41
Dec. 24	2.119	18.71	4.33
〃	2.213	19.76	4.38

Summary

1) A new method for the determination of sulfur in organic compounds has been established.

2) This method is based on the utillization of the reducing power of tin(II)-strong phos-

---

[9] T. Kiba, T. Takagi, Y. Yoshimura and I. Kishi, ibid., 28, 641 (1955).

phoric acid and the oxidizing power of chromium(VI)-strong phosphoric acid.

3) Sulfur in organic compounds is reduced to hydrogen sulfide by heating with tin(II)-strong phosphoric acid directly (Procedure A) or after oxidizing with chromium(VI)-strong phosphoric acid (Procedure B).

4) The liberated hydrogen sulfide is absorbed in zinc acetate solution and estimated by the iodimetry.

5) The analytical results obtained for methylorange, sulfur guanidine, and cystine by the Procedure A and for thiourea, methionine, acetylmethionine, and thionalide by the Procedure B were given.

Acknowledgments are made to Prof. T. Kiba for his interest and encouragement and to Miss. I. Kishi for her helpful assistance. A part of the expence for the experiment has been defrayed from a grant given by the Ministry of Education, to which the author's thanks are due.

Department of Chemistry, Faculty of
Science, Kanazawa University,
Kanazawa