Tin (II)-Strong Phosphoric Acid. A New Reagent for the Determination of Sulfate by Reduction to Hydrogen Sulfide

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Although a number of methods for the determination of sulfate by reduction to hydrogen sulfide have previously been worked out[1], these methods are substantially based on dry heating[2] or fusion[3] of the sulfate-containing substances with adequate reductants. It has long been desired to develop a new method by which soluble or insoluble sulfate can be reduced to hydrogen sulfide in solution with simple treatment and apparatus. E. Rancke-Madsen[4] gives a procedure for the determination of sulfate by reduction to hydrogen sulfide in a mixture of tin (II)-chloride and phosphoric acid. By checking the method according to his procedure the present authors proved that the method can be applied only when the sulfate is present as sodium salt and moreover when the evolved hydrogen chloride on the reduction markedly acidifies the absorbing solution of zinc acetate and acetic acid, over the optimum range of pH that is adopted for zinc sulfide precipitation. C. M. Johnson and H. Nishita[5] reduced sulfates and organic sulfur compounds with a reducing mixture composed of hydroiodic acid, formic acid, and red phosphorus at a temperature of 115°C., and they determined the sulfur in plant materials, soils, and irrigation waters. However the reagents used in the method are not easily obtainable without accompanying impurity of sulfates and sulfur, especially for the purpose of micro-determination of sulfur.

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 carbon[6], oxidation value of organic compounds[7], and nitrogen in organic compounds[8,9], using a strong oxidizing action of potassium iodate in the medium have been already reported. The revealed fact that the strong phosphoric acid scarcely participates in the reaction carried on in it may also be utilized to the reduction by adding an adequate reductant in the medium. A new reagent for the reduction of sulfate to hydrogen sulfide was prepared by adding tin(II)-chloride into the strong phosphoric acid and boiling the mixture to expel the evolved hydrogen chloride perfectly. Very viscous and slightly turbid liquid thus obtained, named "Tin(II)-Strong Phosphoric Acid", can be stored in a desiccator of calcium chloride with slight decrease of reducing power for several months and be used as a conspicuous decomposing and reducing agent by heating above 120°C. for the determination of soluble and insoluble sulfates. In the following a method will be described in which the sulfate is determined by reduction to hydrogen sulfide with the above reagent, including details of preparation of the reagent and construction of apparatus.

Apparatus

The set-up used for the preparation of the strong phosphoric acid and the tin(II)-strong phosphoric acid is illustrated in Fig. 1. For the critical purpose it is profitable to use a flask of fused silica instead of hard glass. A glass tube E plays as an outlet of water vapor in the preparation of strong phosphoric acid and as an inlet of carbon dioxide in the case of the preparation of tin (II)-strong phosphoric acid.

In Fig. 2 the apparatus for the reduction of sulfate and absorption of the evolved hydrogen sulfide is given as the assembly. All of these are hand-made in addition to Kipp's apparatus for production of carbon dioxide. Into the reaction vessel A, a gas-inlet B and a thermometer D, which is covered with a thermometer-protecting tube C, are inserted. These tubes are attached to the reaction vessel with suitable rubber tube as shown in Fig. 2.

Reagents

Strong Phosphoric Acid.—Three hundred gram of commercial orthophosphoric acid of extra pure chemical grade (d=1.7) is placed in a flask in Fig. 1, and dehydrated by heating on a hot plate D, until a thermometer dipped in the liquid

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1 A. Kurtenacker, "Analytische Chemie der Sauerstoffsäuren des Schwefels." Stattgart, (1938).

2) Y. Oka and T. Kanno, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*) 72, 161 (1951).

3) K. Bruger, *Angew. Chem.*, 54, 479 (1941).

4) E. Rancke-Madsen, *Acta. Chim. Scand.*, 3, 773 (1949); 6, 305 (1952).

5) C.M. Johnson and H, Nishita, *Anal. Chem.*, 24, 736 (1952).

6) T. Kiba et al., *Japan Analyst*, 2, 446 (1953).

7) S. Ohashi, This Bulletin, 28, 171 (1955).

8) S. Ohashi, ibid, 28, 177 (1955).

9) S. Ohashi, ibid, 28, 537 (1955).

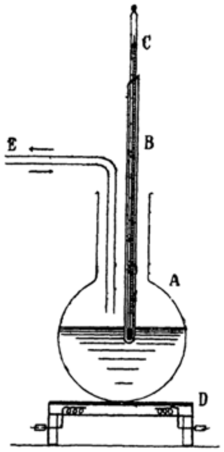

Fig. 1. Apparatus for the preparation of strong phosphoric acid and tin (II)-strong phosphoric acid.

A: Round bottom flask of 400 ml.
B: Thermometer-protecting tube.
C: Thermometer of 360°C.
D: Electric hot plate.
E: Glass tube.

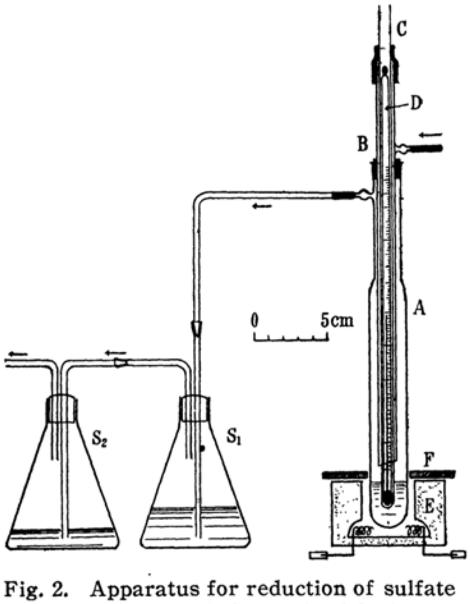

Fig. 2. Apparatus for reduction of sulfate and absorption of the evolved hydrogen sulfide.

A: Reaction vessel.
B: Gass-introducing tube.
C: Thermometer-protecting tube.
D: Thermometer.
E: Electric heater.
F: Asbestos plates·
S_1: Absorbing flask.
S_2: Absorbing flask.

shows 300°C. During the heating evaporated water vapor and mist of phosphoric acid should be rapidly removed from the liquid surface through a glass tube E which is connected to a suction pump. This makes the time for the evaporation shorter and contamination brought from the components of the glass smaller. The very viscous liquid thus obtained, strong phosphoric acid, is stored in a desiccator.

Tin(II)-Strong Phosphoric Acid.—Using the same apparatus shown in Fig. 1 tin(II)-strong phosphoric acid is prepared as follows. Twenty to eighty grams of crystals of tin(II)-chloride dihydrate of extra pure chemical grade, the amout of which is dependent upon that of sulfate to be analyzed, is placed in a flask A and covered with 200 g. of strong phosphoric acid obtained above. Introducing purified carbon dioxide from a Kipp's apparatus through a tube B, the content is gently heated to 300°C. Hydrogen chloride gas is evolved by the reaction and sometimes brownish color appears in the liquid. The color may be caused by the formation of tin(II)-sulfide, because a small quantities of sulfate which has been contained originally in commercial phosphoric acid as impurity or comes from the glass wares during the reaction are all reduced to hydrogen sulfide. In this case the temperature should be kept at 300°C. till the color disappears. The contents should be cooled under continuous passing of carbon dioxide. The obtained tin(II)-strong phosphoric acid can be stored in a desiccator of calcium chloride for several months.

Zinc Acetate Solution.—Dissolve 40 g. of zinc acetate dihydrate in distilled water of 100 ml. and add 30 ml. of gracial acetic acid,and dilute to 1 liter.

Iodine, 0.02N. Standardized accurately by ordinary procedure.

Sodium Thiosulfate, 0.02N. Standardized accurately.

Various Sulfates Samples. An aliquot from solution of a definite volume in which a known amount of sulfate has been dissolved, and a weighed sample of insoluble sulfate as barium sulfate are both used. The amounts of the sulfate ion in the sample were estimated gravimetrically as comparable standards.

Procedure

Pipet accurately an aliquot from solution of sulfate as it contains 5 to 20 mg. of sulfate ion, or weigh 10 to 25 mg. of barium sulfate into the reaction vessel A in Fig. 2. The solution should be evaporated to dryness at the bottom of the vessel. From a buret pour about 6 to 10 ml. of tin(II)-strong phosphoric acid in the vessel; then connect all of the apparatus as shown in Fig. 2. In the absorbing flasks zinc acetate-acetic acid solution was previously added as 40 ml. in S_1 and 20 ml. in S_2. Pass carbon dioxide very rapidly through the apparatus for five minutes. The passage of the gas should be rapid enough to cause strong agitation of the surface of the liquid in the absorbing flasks. At the end of five minutes reduce the flow of carbon dioxide to a rate of 120 bubbles per minute in the absorbing flask. Gently heat the bottom of the reaction vessel A on a small electric heater E. Gas begins to evolve from the bottom of the vessel when the temperature reaches 120°C. Continue the heating till it reaches 300°C. for about fifteen minutes, and then stop the heating. Carbon dioxide should be passed continuously through the apparatus to carry away the evolved hydrogen sulfide completely. Disconnect the absorbing flask from the side arm of the reaction vessel, add quickly 20 ml. of 0.02N iodine solution to the absorbing flask through the inlet tube, and swirl to mix thoroughly. Because some zinc sulfide may cling to the inlet tube of the absorbing flask, keep this tube in the absorbing flask when treating with the reagent. Back titrate the excess of iodine with 0.02N sodium thiosulfate solution using starch as indicator. The whole determination can be carried out in one hour. Further some blank tests are run by adding no sulfate. 1 ml. of 0.02N iodine consumed corresponds to 0.9607 mg. of SO_4, 0.3408 mg. of H_2S, and 0.3206 mg. of S, respectively.

Results and Discussion

Composition of Tin(II)-Strong Phosphoric Acid.—Though the reagent has a remarkable reducing power, it is questionable from what component the reducing power occurs. In consequence of the reaction between tin(II)-chloride and strong phosphoric acid, not only stannous ion but phosphorous acid as well as hypophosphorous acid may be existing in the reagent. In order to estimate the composition of the tin(II)-strong phosphoric acid, the following experiment was carried out. A definite volume of tin(II)-strong phosphoric acid that has been prepared from 200 g. of strong phosphoric acid and 20 g. of tin(II)-chloride was weighed and dissolved in an adequate volume of 1.5N hydrochloric acid, and then titrated rapidly with 0.1N iodine solution using starch as indicator. The required volume of the iodine solution may correspond to the amount of stannous ion in the solution. The titrated solution was followed by the determination of phosphorous acid and hypophosphorous acid according to the method of E. H. Swift[10], in which each of them is estimated separately by iodometric titration at the different pH. The consumed volume of 0.1N iodine solution by each component of stannous ion, phosphorous acid, and hypophosphorous acid are tabulated in Table I. This indicates that the reducing power of the tin(II)-strong phosphoric acid is most attributed to stannous ion in it.

TABLE I

CONSUMED VOLUME OF 0.1N IODINE SOLUTION BY THREE COMPONENTS OF REDUCTANT IN TIN(II)-STRONG PHOSPHORIC ACID (FOR 1.4915 g. OF THE ACID)

No.	0.1N Iodine Consumed. ml.		
	Sn^{++}	H_3PO_3	H_3PO_2
1	10.73	2.51	1.05
2	10.72	0.13	3.09
3	10.34	0.16	0.44

Stability of Tin(II)-Strong Phosphoric Acid.—Because tin(II)-strong phosphoric acid has an excellent reducing power only above the temperature of 120°C., it may be considered as a very convenient reductant from the point of view of its storage. The decrease of the reducing power during standing at the room temperature of about 30°C. was estimated as a consumable volume of 0.02 N iodine solution by a definite volume of hydrochloric acid solution of 0.1 g. of tin(II)-strong phosphoric acid. For an example on 29th July, 1954, 4.65 ml. of the iodine solution was required and on 1st September, 4.07 ml., so the decrease rate of the reducing power is computed as 10% in a month but smaller in the cold.

Determinable Amount of Sulfate.—The recovery of sulfate as hydrogen sulfide by this method might be dependent upon both of the amounts of sulfate to be analyzed and that of tin(II)-strong phosphoric acid used as the reductant. To estimate the optimum range of quantitative recovery of sulfate the following experiments were carried out. Taking various aliquots from the working standard solution which contains 1 mg. of SO_4 in 1.00 ml. as sodium sulfate, the determination was worked for each of them using 6 and 10 ml. of tin (II)-strong phosphoric acid that has been prepared from 200 g. of strong phosphoric acid and 50 g. of stannous chloride dihydrate. The recovery of sulfate of various amount is illustrated in Fig. 3, in which the

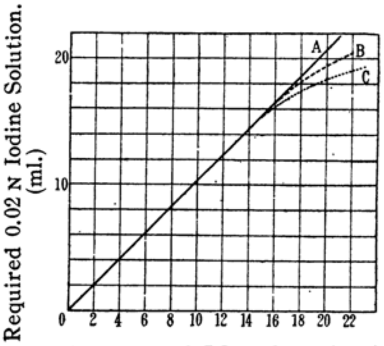

Fig. 3. Range of quantitative recovery of sulfate, using tin (II)-strong phosphoric acid prepared from 200 g. of strong phosphoric acid and 50 g. of $SnCl_2 \cdot 2H_2O$.

A: Theoretical.
B: Using 10 ml. of the reagent.
C: Using 6 ml. of the reagent.

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[10] E.H. Swift, *Anal. Chem.*, 25, 1272 (1953).

ordinate indicates the values of 0.02N iodine solution required for titration of evolved hydrogen sulfide in ml. and the abscissa mg. of sulfate ion taken. In both cases the optimum range for the quantitative recovery of sulfate covers from 0 to 15 mg. of sulfate ion, so the substances to be analyzed should be taken as the amount of its sulfate ion which falls within the above range. The range will be extended to a larger amount of sulfate when we can prepare the tin(II)-strong phosphoric acid which contains a larger quantity of stannous ion. The problem is now being unraveled in the laboratory.

Analytical Applications.—Analyses of various sulfates were made with this method. These results are summarized in Table II.

TABLE II

DETERMINATION OF VARIOUS SULFATES

Substance	Sample Weight mg.	SO_4 Content mg.	0.02 N Iodine Required ml.	SO_4 Found mg.
Sodium sulfate Na_2SO_4	10.41	7.03	7.30	7.01
	5.20	3.51	3.64	3.50
	9.94	6.71	6.96	6.69
	9.94	6.71	6.96	6.69
	9.94	6.71	7.06	6.78
Alum $KAl(SO_4)_2\cdot 12H_2O$	25.73	10.42	10.88	10.45
	〃	〃	10.82	10.40
	〃	〃	10.78	10.36
	〃	〃	10.87	10.44
Chrome alum $KCr(SO_4)_2\cdot 12H_2O$	26.00	10.00	10.48	10.07
	〃	〃	10.49	10.08
	〃	〃	10.49	10.08
Zinc sulfate $ZnSO_4\cdot 7H_2O$	31.22	10.43	10.86	10.43
	〃	〃	10.80	10.38
	33.37	11.15	11.15	11.09
	〃	〃	11.15	11.09
	62.44	20.86	21.69	20.84
Magnesium sulfate $MgSO_4\cdot 7H_2O$	30.52	12.46	12.22	11.74
	〃	〃	12.21	11.73
	〃	〃	12.24	11.76
Barium sulfate $BaSO_4$	12.12	4.98	5.13	4.94
	23.20	9.55	9.73	9.35
	24.70	10.16	9.70	9.32

Each of the weighed samples of sodium sulfate, alum, chrome alum, zinc sulfate, and magnesium sulfate was dissolved in water of a constant volume and pipetted into the reaction vessel as an aliquot of the solution. The pipetted solution in the vessel was evaporated to dryness and allowed to be analyzed. On the other hand, the content of sulfate ion in each of the solutions had been determined gravimetrically as barium sulfate as usual. As an example of insoluble sulfates, barium sulfate was analyzed by this method. The sample was weighed accurately using a micro-balance and allowed to be analyzed in the reaction vessel directly. The precision and accuracy of the data were subject to slight fluctuations with the kind of sulfate, but the errors rested within that of the usual gravimetric method. Further determinations were also carried out on other sulfates, like cupric sulfate and that of the second group metals, but the results were so much worse than those in Table II that only half of the sulfate ion could be reduced. The investigation on this fact and its cause is now being done in the laboratory. In the near future we will be able to report a more consummate method adoptable for all sulfates.

Summary

A new reagent, " Tin(II)-Strong Phosphoric Acid ", has been prepared to permit a rapid and simple determination of sulfates by reducing to hydrogen sulfide. The reagent is stable at a room temperature but reacts violently above 120°C. Evolved hydrogen sulfide after the reaction with this reagent is absorbed in zinc acetate-acetic acid solution and titrated iodometrically as usual. 1 ml. of 0.02N iodine solution corresponds to 0.9607 mg. of sulfate ion. The apparatus for the preparation of the reagent and reduction of sulfate are illustrated. The determination of sulfur in various sulfates was carried out by this method and satisfactory results were obtained. Moreover, it seems to be an advantage of this method that solid samples can be treated directly in the reaction vessel.

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