Determination of Sulfate by Means of Metal-Polyphosphate Reduction Method

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Various methods for the estimation of sulfate by reduction to hydrogen sulfide have been known, and recently Madsen[1)], Johnson[2)], Kiba[3)], and Ohashi[4)] have given procedures for volumetric determination of sulfate. Madsen used a mixture of tin (II) chloride and phosphoric acid as reductant. But his method is applicable only to the determination of sodium sulfate. Johnson and Nishita[2)] have shown methods for micro determination of sulfur, sulfate and organic sulfur compounds using a reducing mixture of hydroiodic acid and red phosphorus at 115°C. Kiba gives a new procedure involving the use of tin (II)-strong phosphoric acid mixture. By his method, sulfur in barium, magnesium, sodium and zinc sulfate as well as aluminium and chromium alum, are estimated. Ohashi reported also on the rapid determination of sulfur in organic compounds by means of the tin(II)-strong phosphoric acid method. According to his method, nitro compounds are determined within 0.5 % accuracy. On the other hand, a few applications of triphosphate have been reported by the present authors. In the present paper, will be described the determination of soluble and insoluble sulfate by means of new reducing agents, metal-polyphosphate systems: titanium(III), chromium(II), molybdenum(IV), tungsten (V), and vanadium(IV), pyrophosphate, triphosphate and mixed polyphosphate systems.

Equipment and Material

Equipment.—The apparatus for reduction of sulfate consists of two parts, (A) reduction- and (B) absorption- vessel. For the former a 50 ml. pear-shaped flask is used in a reaction below 120°C or a 10 ml. porcelain boat between 700°C and 900°C. The flask is provided with one glass tube for introduction of carbon dioxide and another one, through which the resultant gas mixture can be drawn to the absorption vessels. The boat is inserted into a silica tube, (length, ca. 40 cm. diameter, ca. 2 cm.) which is provided also with gas inlet- and delivery- tube as mentioned above. For the latter three 150 ml. flasks connected to each other with ruber tubings are used; the first is a gaurd flask and the remaining two are for absorption. A porcelain crucible No.5 is used for fusion of the mixture of polyphosphate and powdered metal.

Material.—Sodium sulfite, and barium, lead, and sodium sulfate were used as samples. The purity of lead and sodium sulfate was determined gravimetrically, while sodium sulfite was estimated iodimetrically. Barium sulfate was prepared from barium chloride and potassium sulfate.

Standard Solution.—One tenth normal potassium triiodide solution was used as absorbent, and sodium thiosulfate solution of the same normality as a reference standard solution. No indicator was used in the titration.

Titanium Polyphosphate Systems. — (a) Five g. of metallic titaninm is added to 200 g. of orthophosphoric acid (sp. gr. 1.86), which is boiled to dissolve the metals. Titanium is oxidized to tervalent state; even if colorless quadrivalent ion should be formed here, it would be reduced to tervalent state by the elementary one. Tervalent titanium in polyphosphate is very stable in the cold and has a vigorous reducing force at high temperatures. In separate experiments, 0.3 g. portions of titanium are dissolved in mixtures containing each 5 g. of orthophosphoric acid, (sp. gr. 1.83) along with (b) 2.5 g. of pyrophosphate, (c) 2.5 g. of triphosphate, (d) 2.5 g. of hexametaphosphate, and (e) 5g. of a mixture of the hexameta- and tri- phosphate in equal proportion respectively; (a) and (b) are used at 200°C, while (c), (d) and (e) at 700°—900°C.

Chromium-, Manganese-, Molybdenum-, and Tungsten- Polyphosphate Systems.—Metallic chromium is dissolved in phosphoric acid; the solution which exerts a reducing force at a high temperature, contains the metal in bivalent and tervalent state and is of green color. Chromium-polyphosphate reducing systems as well as those containing manganese, molybdenum and tungsten are prepared as in the case of titanium.

Vitreous Polyphosphates. — Mixtures prepared from phosphoric acid and pyro-, tri- and hexa- phosphate without the additon of metals are used as diluents.

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1) E. R. Madsen, *Acta. Chim. Scand.*, **3**, 773 (1949); **6**, 305 (1952).

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

3) T. Kiba, This Bulletin, **28**, 641 (1955).

4) S. Ohashi, This Bulletin, **28**, 645 (1955).

Procedure

Place a sample of approximately 0.01 g. of air dry sulfate in the reduction flask or in the ignition boat. Add ca. 7 g. of reducing metal-polyphosphate mixture. To each absorber for hydrogen sulfide, add 25 ml. of one tenth normal potassium triiodide solution and 20 ml. of water. Pass a current of carbone dioxide for at least 2 minutes through the reduction flask or the silica tube into which the ignition boat is inserted, in order to remove atmospheric oxygen. Allow the reaction to proceed gradually at a boiling temperature of the mixture in the current of carbon dioxide for about 20 minutes. After heating, the potassium triiodide solution, in which hydrogen sulfide gas is absorbed, is titrated with standard sodium thiosulfate solution. One ml. of one tenth normal solution of sodium thiosulfate corresponds to 7.103 mg. of sodium sulfate, 6.9043 mg. of sodium sulfite, 14.377 mg. of zinc sulfate monohydrate, 15.164 mg. of lead sulfate and 11.671 mg. of barium sulfate.

Result and Discussion

Titanium Polyphosphate Systems.—(1) When barium, lead, or sodium sulfate is treated with H_3PO_4–Ti reducing system at about 200°C for 15–20 minutes, it is reduced to sulfide; the evolved hydrogen sulfide is absorbed in standard potassium triiodide solution and the excess of triiodide is titrated with standard sodium thiosulfate solution. The results are satisfactory as shown in Table I. Sodium sulfite can not be reduced, however, to sulfide by this reducing system, presumably because the sulfide is easily decomposed by the heat treatment, and the resultant sulfur volatilizes at a high temperature. The results are shown in Table I.

TABLE I

H_3PO_4–Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	20	blanck	0.0
	15	12.2	11.8
	〃	30.4	29.9
	〃	61.9	61.1
	25	123.6	101.1
$PbSO_4$	15	33.4	33.9
$BaSO_4$	15	28.6	28.0
	〃	32.3	31.9
	20	61.7	62.3
	30	97.4	81.8
	〃	122.3	95.5
Na_2SO_3	20	29.5	29.4
	30	67.9	62.8

(2) Solid samples of sulfates are reduced also by means of H_3PO_4–$(HPO_3)_6$–Ti system. In this case, the samples are heated at a higher temperature, about 200°C. for 15 minutes. The results are shown in Table II. A small quantity of sodium sulfite is reduced completely, but such is not the case with its large amount.

TABLE II

H_3PO_4-$(HPO_3)_6$-Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	15	46.8	46.4
	〃	83.7	83.9
$PbSO_4$	〃	40.1	40.4
$BaSO_4$	〃	27.0	26.9
Na_2SO_3	〃	18.1	17.8

(3) When H_3PO_4–$Na_5P_3O_{10}$–Ti system is used as a reducing agent, sulfates are determined satisfactorily as shown in Table III. Nevertheless it must be recognized that their large amounts can not be completely reduced by this method. This owes to the fact that the reaction temperature is higher than in other cases.

TABLE III

H_3PO_4-$Na_5P_3O_{10}$-Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	10	27.4	27.2
	15	57.9	57.5
	〃	91.3	82.1
$PbSO_4$	〃	60.9	61.1
	〃	102.4	94.3
$BaSO_4$	〃	68.5	68.3
	〃	102.0	100.4
Na_2SO_3	10	32.8	32.6
	15	31.0	30.9
	〃	63.0	53.9

TABLE IV

H_3PO_4-$NaPO_3$-Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
H_2SO_4	25	21.1	21.6
K_2SO_4	15	22.0	21.8
$PbSO_4$	〃	24.6	24.4
$BaSO_4$	〃	23.0	23.2
Na_2SO_3	〃	9.5	9.6

(4) The same fact is also observed in H_3PO_4–$NaPO_3$–Ti reducing system. About 20 mg. of sulfate are treated with the reductant in a pear-shaped flask for about

15 minutes, and found to be reduced completely, but a sample weighing more than 20 mg. can not be determined satisfactorily. The results are shown in Table IV.

(5) A reducing agent prepared from H_3PO_4, HPO_3, $Na_5P_3O_{10}$ and metallic titanium is used at about 700°C. The reaction velocity being still small, the result after 20 minutes' heating is unsatisfactory; one hour is necessary for complete reduction. The results are shown in Table V.

TABLE V

H_3PO_4-$(HPO_3)_6$-$Na_5P_3O_{10}$-Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	20	32.3	29.3
	60	36.5	36.7
$PbSO_4$	20	35.8	30.4
	60	57.8	57.8
$BaSO_4$	20	34.1	29.7
	60	45.9	45.7
Na_2SO_3	20	34.5	25.1
	40	30.0	25.1
	60	38.4	33.0

(6) Table VI shows the results obtained from reactions between H_3PO_4–$Na_4P_2O_7$–Ti reducing agent and sulfates. The reacting mixture is heated in the boat at 800°C; one hour's heating is necessary.

TABLE VI

H_3PO_4-$Na_4P_2O_7$-Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	30	22.0	16.4
	60	29.0	28.7
$PbSO_4$	30	32.1	32.6
	60	37.4	37.6
$BaSO_4$	30	42.1	37.6
	60	41.9	41.7
Na_2SO_3	30	21.3	16.4
	60	20.4	17.8

TABLE VII

H_3PO_4-$(HPO_3)_6$-$KNaCO_3$-Ti SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	30	16.6	11.1
	60	12.3	12.2
$PbSO_4$	30	17.9	12.2
	60	13.5	13.6

(7) When potassium-sodium carbonate is added to the reducing system, its melting point rises, which makes the treatment of reducing reaction more difficult. When heated for 60 minutes however, sulfates are satisfactorily determined as shown in Table VII.

Other Metal-Polyphosphate Systems.—(8) H_3PO_4–$Na_5P_3O_{10}$–metal systems. Metallic chromium, manganese, molybdenum or tungsten are dissolved by heating in a mixture of phosphoric acid and sodium triphosphate, and used as reducing agent. But the results of the estimation are satisfactory only in the case of the chromium system as shown in Table VIII.

TABLE VIII

H_3PO_4-$Na_4P_2O_7$-Cr SYSTEM

Sample form	Heating time (min.)	Sample mg.	
		Content	Found
K_2SO_4	15	34.2	34.2
$PbSO_4$	〃	35.7	35.4
$BaSO_4$	〃	30.7	30.7

(9) In order to increase acidic properties and rise the melting point, metaphosphate is added to this system; the sulfate is completely reduced by the reductant as shown in Table IX. These estimations required a heating period of 1 hour.

TABLE IX

H_3PO_4-$(HPO_3)_6$-Na_3PO_4-METAL SYSTEMS

Metal	Sample form	Heating time (min.)	Sample mg.	
			Content	Found
Cr	K_2SO_4	30	11.7	10.1
		60	10.8	10.9
	$PbSO_4$	30	10.7	10.2
		60	11.9	11.8
	$BaSO_4$	30	10.0	7.8
		60	10.4	10.4
Mn	K_2SO_4	30	12.3	11.3
		60	13.4	13.5
	$PbSO_4$	30	17.0	16.2
		60	23.4	23.3
	$BaSO_4$	30	10.7	9.7
		60	16.5	16.5
Mo	K_2SO_4	30	15.6	13.1
		60	20.1	20.1
	$PbSO_4$	30	20.2	19.8
		60	19.2	19.2
	$BaSO_4$	30	15.8	13.3
		60	17.8	18.0
W	K_2SO_4	30	11.6	11.0
		60	11.7	11.8
	$PbSO_4$	30	20.0	16.5
		60	10.0	10.0
	$BaSO_4$	30	10.0	7.7
		60	10.0	10.0

(10) Prolonged heating is also required in the HPO_3–H_3PO_4–$KNaCO_3$–metal system. Sulfates are completely reduced to sulfide by heating for 1 hour with these reducing agents, and the results are shown in Table X.

TABLE X

H_3PO_4-$(HPO_3)_6$-$KNaCO_3$-METALS SYSTEMS

Metal	Sample form	Heating time (min.)	Sample mg.	
			Content	Found
Cr	K_2SO_4	30	12.4	11.5
		60	11.0	11.0
	$PbSO_4$	30	13.7	11.3
		60	10.7	10.7
	$BaSO_4$	30	13.5	12.6
		60	14.3	14.3
Mn	K_2SO_4	30	23.9	21.1
		60	18.8	18.4
	$PbSO_4$	30	21.2	18.8
		60	20.7	20.7
	$BaSO_4$	30	21.7	14.0
		60	15.7	15.7
Mo	K_2SO_4	30	10.6	9.1
		60	10.0	9.9
	$PbSO_4$	30	10.7	9.0
		60	13.8	13.8
	$BaSO_4$	30	13.0	12.5
		60	11.3	11.3
W	K_2SO_4	30	13.2	9.9
		60	10.0	9.9
	$PbSO_4$	30	13.2	12.4
		60	12.2	12.1
	$BaSO_4$	30	10.0	7.5
		60	11.7	11.6

(11) H_3PO_4–$Na_5P_3O_{10}$–metal systems are also used as reducing agents for sulfates, as shown in Table XI. In these systems, chromium is assumed to be present mainly as bivalent, molybdenum as tervalent, manganese as bivalent, and tungsten as quadrivalent compounds respectively, to which the reducing property of the systems is due.

TABLE XI

H_3PO_4-$Na_5P_3O_{10}$-METALS SYSTEMS

Metal	Sample form	Heating time (min.)	Sample mg.	
			Content	Found
Cr	K_2SO_4	30	14.3	12.7
		60	10.4	10.4
	$PbSO_4$	30	9.8	8.3
		60	10.1	10.2
	$BaSO_4$	30	10.4	8.9
		60	10.0	10.0
Mo	K_2SO_4	30	15.9	14.0
		60	16.0	16.0
	$PbSO_4$	30	14.6	13.6
		60	10.6	10.6
	$BaSO_4$	30	10.8	9.1
		60	15.8	15.8
W	K_2SO_4	30	10.0	8.3
		60	11.8	11.8
	$PbSO_4$	30	15.9	13.3
		60	11.0	10.9
	$BaSO_4$	30	9.6	8.1
		60	11.0	10.9

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