

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

## The Coprecipitation of Barium Ion with the Sulfides of the Ammonium Sulfide Group in the Presence of Ammonium Ion

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It is a well-known fact that considerable amounts of barium ion are lost in systematic qualitative analysis.<sup>1</sup> When the ammonium sulfide group is precipitated, this loss has been attributed to the precipitation of barium carbonate and sulfate, the former by absorption of carbon dioxide and the latter by oxidation of sulfide ion.<sup>1a,b</sup> However it has recently been shown that in the precipitation of hydrous aluminum, chromic and ferric oxides, the loss of barium ion is not due to the formation of barium carbonate but to a combination of effects, *viz.* adsorption, occlusion, and post-precipitation.<sup>1c</sup> Later, in the experimental part of this paper, it will be demonstrated that no oxidation of sulfide to sulfate ion occurs when the sulfides are precipitated.

Sulfide precipitates, when first formed, are usually either amorphous or microcrystalline.<sup>2</sup> Therefore, in the alkaline solution where the sulfides would be negatively charged, surface adsorption of barium ion might occur. Zolotukhin says<sup>1b</sup> that adsorption causes a loss of barium ion, but no definite evidence is given to confirm this statement. That sulfides "induce" precipitation of metal ions has already been shown in the case of sulfides of the copper group by Kolthoff and his co-workers.<sup>3</sup>

The purpose of our work was to determine the cause of the retention (loss) of barium ion. Only after this was known might it be possible to prevent or overcome this loss.

### Experimental

The conditions under which the experimental work was done were the same as in our previous paper, except that in a number of experiments centrifuging was used instead of filtering.

**Determination of Sulfate Ion when Sulfides are Precipitated by Ammonium Sulfide in the Presence of Ammonium Chloride.**—To a solution containing 100 mg. of each of the metal ions of the ammonium sulfide group,

(1) (a) Curtman and Frankel, *THIS JOURNAL*, **33**, 724 (1911); (b) Zolotukhin, *Acta Univ. Vorogensis*, **9**, 69 (1937); (c) Lehrman, Been and Manes, *THIS JOURNAL*, **62**, 1014 (1940).

(2) Kolthoff and Moltzau, *Chem. Rev.*, **17**, 307 (1935).

(3) (a) Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932); (b) Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935); (c) Kolthoff and Moltzau, *J. Phys. Chem.*, **40**, 779 (1936); (d) Kolthoff, Griffith and Moltzau, *THIS JOURNAL*, **60**, 1576 (1938); (e) Kolthoff and Griffith, *ibid.*, **60**, 2038 (1938).

except aluminum and chromium, was added 1 g. of ammonium chloride, 10 ml. of 15 *M* ammonia and enough water to make the volume 50 ml. Then hydrogen sulfide was passed in until complete precipitation took place. The mixture was filtered and divided into three parts. One portion was tested directly for sulfate ion by acidifying with 3 *M* hydrochloric acid, filtering off any sulfur that formed, concentrating the filtrate and adding barium chloride solution. The result showed no sulfate ion. The second portion was acidified with 6 *M* acetic acid, allowed to stand exposed to the air for five days, filtered to remove any sulfur that formed, the filtrate concentrated and barium chloride solution added. The result showed no sulfate ion. The third portion was allowed to stand exposed to the air for five days and after acidifying with 3 *M* hydrochloric acid, the same procedure as above was carried out. The result showed no sulfate ion.

In order to find out if any sulfate ion is present in the sulfide precipitate, the following experiment was performed. A solution containing 100 mg. each of ferric, manganous and zinc ions, 1 g. of ammonium chloride, 10 ml. of 0.02% gelatin solution,<sup>4</sup> 10 ml. of 15 *M* ammonia in a total volume of 50 ml. was treated with hydrogen sulfide until complete precipitation took place. The mixture was filtered through quantitative filter paper and the precipitate washed free of hydroxyl ion. Then 3 *M* hydrochloric acid was repeatedly poured over the precipitate until it completely dissolved. The solution was evaporated just to dryness, the residue dissolved in a small volume of water and barium chloride solution added. The result showed an extremely small amount of sulfate ion.

In order to find out if any barium sulfate forms should barium ion be present during the precipitation of the sulfides, the previous experiment was repeated with the addition of 40 mg. of barium ion to the solution. After the sulfides had been dissolved, the filter paper was washed free of chloride ion, ignited in a weighed crucible to an ash, a few drops of 36 *M* sulfuric acid added and reheated to constant weight. The result was a negligible amount of ash, which gave no flame test for barium.

On the basis of the results of the above experiments, the conclusion can be drawn that no sulfate ion is formed when the sulfides of the ammonium sulfide group are precipitated.

**Retention of Barium Ion by the Individual Sulfides of the Ammonium Sulfide Group.**—To separate solutions containing 100 mg. of each of the metal ions, except aluminum and chromium, 1 g. of ammonium chloride, 5 ml. of 0.02% gelatin solution, 8, 16, 24, 32 and 40 mg. separately of barium ion, and 7 ml. of 15 *M* ammonia in a total volume of 25 ml., hydrogen sulfide was passed in until complete precipitation took place. The mixtures were centrifuged

(4) The gelatin made it possible to wash the precipitate with distilled water with very little peptizing action. Caldwell and Moyer, *ibid.*, **57**, 2372 (1935).

TABLE I

EFFECT OF VARYING AMOUNTS OF AMMONIUM CHLORIDE AND THE ADDITION OF BARIUM ION AFTER THE PRECIPITATION OF THE SULFIDES ON THE AMOUNT RETAINED

Metal, mg.	NH <sub>4</sub> Cl, g.	Ba <sup>++</sup> , when added	Ba <sup>++</sup> in filtrate, mg.	Ba <sup>++</sup> retained, mg.
150 Ni <sup>++</sup> and Co <sup>++</sup> , 200 Zn <sup>++</sup>	1	Before pptn.	19	21
150 Ni <sup>++</sup> and Co <sup>++</sup> , 200 Zn <sup>++</sup>	4	Before pptn.	34	6
75 Ni <sup>++</sup> and Co <sup>++</sup> , 100 Zn <sup>++</sup>	1	Before pptn.	30	10
75 Ni <sup>++</sup> and Co <sup>++</sup> , 100 Zn <sup>++</sup>	4	Before pptn.	37	3
150 Ni <sup>++</sup> and Co <sup>++</sup> , 200 Zn <sup>++</sup>	1	After pptn.	24	16
150 Ni <sup>++</sup> and Co <sup>++</sup> , 200 Zn <sup>++</sup>	4	After pptn.	35	5
500 Fe <sup>+++</sup>	1	Before pptn.	13	27
500 Fe <sup>+++</sup>	4	Before pptn.	24	16
500 Fe <sup>+++</sup>	1	After pptn.	19	21
500 Fe <sup>+++</sup>	4	After pptn.	34	6

and the precipitates washed until no test for barium ion was obtained. Usually three washings sufficed. The centrifugates were evaporated to a small volume, centrifuged if not clear, and the barium ion precipitated with ammonium sulfate in special tubes.<sup>5</sup> The amount of barium in the precipitates was determined, after the tubes had stood for one week, by measuring the height of the barium sulfate and comparing it with the height of known amounts of barium sulfate precipitated under the same conditions in similar tubes.<sup>1c</sup>

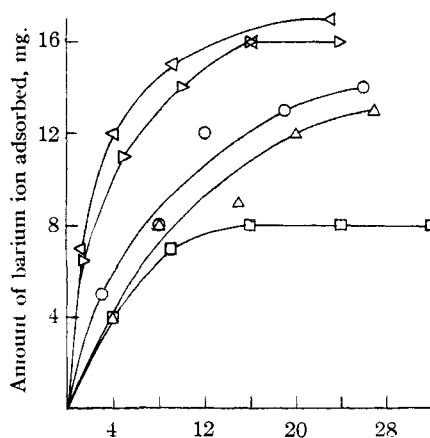
Figure 1 is the graph obtained by plotting the amount of barium ion found in the filtrate as abscissa and the amount retained by the different sulfides as ordinates. It is a typical Freundlich isotherm, probably showing adsorption, inasmuch as the precipitations take place under fairly constant conditions, thus yielding an adsorbent of constant specific surface area (*i. e.*, surface per unit mass of adsorbent).

In order to determine what effect, if any, a higher concentration of ammonium ion would have on the retention of barium ion, those experiments using 40 mg. of barium ion were repeated with 4 g. of ammonium chloride instead of 1 g. Corresponding experiments, using 1 g. and 4 g. of ammonium chloride, were carried out on similar solutions, except that the metal ion consisted of a mixture of 150 mg. each of nickel and cobalt ions, and 200 mg. of zinc ion, and in another, one-half this metal ion concentration. The purpose of the latter two experiments was to see if any unusual condition, with respect to saturation of the surfaces of the mixed sulfides with barium ion, takes place as in the case of the mixed hydrous oxides.<sup>1c</sup> For comparison, the previous experiment was repeated with 500 mg. of ferric ion.

The results showed in every case that less barium ion is lost when the concentration of ammonium ion is higher. In an experiment in which the mixed sulfides were precipitated in a solution saturated with ammonium chloride, some barium ion is still retained by the precipitate. Table I contains some of the results.

**Effect of Adding Barium Ion After the Precipitation of the Sulfides on the Amount Retained.**—The previous experiments were repeated, except that 40 mg. of barium ion was added immediately after the precipitation of the sulfides and then the amount of barium ion in the filtrate

determined. Some of the results, together with those of similar experiments above, are shown in Table I.



Amount of barium ion in filtrate (equilibrium solution), mg.

Fig. 1.—Adsorption isotherms of barium ion with the sulfides of the ammonium sulfide group in the presence of 1 g. of ammonium chloride: O, zinc sulfide; □, manganese sulfide; ▷, nickel sulfide; △, ferric sulfide; ◁, cobalt sulfide.

The results showed in every case that less barium ion is retained if it is added after the precipitation of the sulfides than when present in the original solution. No unusual condition with respect to saturation of the surfaces of the precipitates with barium ion occurs as was found in the case of the hydrous oxides.

**Effect of Aging the Sulfides in the Presence of Barium Ion on the Amount Retained.**—Into solutions containing 100 mg. each of nickel, cobalt, manganese and zinc ions and 500 mg. of ferric ion, separately, 1 g. of ammonium chloride, 40 mg. of barium ion, 5 ml. of 0.02% gelatin solution and 7 ml. of 15 M ammonia in a total volume of 25 ml., hydrogen sulfide was passed until complete precipitation took place. The solutions were allowed to stand in airtight, stoppered flasks for six days. Then the amount of barium ion not retained by the precipitates was determined as previously described. The results are shown in Table II.

It is seen that aging the sulfides of nickel, cobalt and manganese in the presence of barium ion increases the

(5) Curtman, "Qualitative Chemical Analysis," revised edition, The Macmillan Co., New York, N. Y., 1938, p. 298.

TABLE II  
EFFECT OF AGING THE SULFIDES IN THE PRESENCE OF  
BARIUM ION ON THE AMOUNT RETAINED

Metal, mg.	Days aged	Ba <sup>++</sup> in filtrate, mg.	Ba <sup>++</sup> retained, mg.
100 Ni <sup>++</sup>	0	24	16
100 Ni <sup>++</sup>	6	2.5	37.5
100 Co <sup>++</sup>	0	23	17
100 Co <sup>++</sup>	6	1.5	38.5
100 Mn <sup>++</sup>	0	32	8
100 Mn <sup>++</sup>	6	4.5	35.5
100 Zn <sup>++</sup>	0	26	14
100 Zn <sup>++</sup>	6	27	13
500 Fe <sup>+++</sup>	0	13	27
500 Fe <sup>+++</sup>	6	19	21

amount retained to a very large extent; in the case of zinc sulfide about the same amount of barium ion is lost after aging as before; while with ferric sulfide less barium ion is retained after aging. It is interesting to note that a similar result was obtained on aging hydrous ferric oxide.<sup>1c</sup>

### Discussion

From the results of the first group of experiments, it is evident that no sulfate ion is formed when the sulfides of the ammonium sulfide group are precipitated. Thus the loss of barium ion cannot be due to the formation of barium sulfate.

When sulfides are precipitated in an alkaline medium, they have a negative charge and therefore favor the adsorption of cations. This fact, together with the nature of the sulfides when first formed, and the typical Freundlich isotherms obtained in Fig. 1, shows that the loss of barium ion is probably due to adsorption. With increasing concentrations of ammonium ion, less barium ion is retained, due to replacement of the latter by the former ion. Yet in a solution saturated with ammonium ion, some barium ion is still lost. Incomplete replacement of barium by ammonium ion in the surface of the precipitates or occlusion of barium ion as the sulfides are forming, could account for this result. That adsorption of an ion is reduced when some other substance is present which can also be adsorbed, has already been shown in the case of a sulfide<sup>6a</sup> and hydrous oxides, especially with ammonium ion.

If the loss of barium ion is due only to surface

(6) (a) Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., Inc., New York, N. Y., 1st ed., 1926, p. 406; (b) Charriou, *J. Chem. Phys.*, **23**, 621 (1926); (c) Kolthoff and Stenger, *J. Phys. Chem.*, **36**, 2113 (1932); (d) Kolthoff and Moskovitz, *ibid.*, **41**, 629 (1937); (e) Kolthoff and Overholser, *ibid.*, **43**, 767, 909 (1939); (f) Lehrman, Been and Manes, *THIS JOURNAL*, **62**, 1014 (1940).

adsorption, then it will be the same whether the barium ion is present before precipitation or added immediately after. However, should barium ion be retained inside the precipitate (occlusion or inner adsorption) while it is forming, less would be lost if it is added after precipitation than if present before. The results show that there is some loss by occlusion.

When a precipitate is allowed to remain in the medium from which it formed, two different effects may take place which would change the amount of an ion retained. As the aging proceeds, crystal growth and perfection result and occluded material is returned to the solution. At the same time, if post precipitation occurs, the amount of ion retained will be increased. Should both these opposite phenomena take place, the final result would depend on which one was greater. As occlusion of barium ion is small, it is obvious from the results of Table II that post precipitation of barium ion with nickel, cobalt and manganese sulfides is very large. In the case of zinc sulfide, since there is very little change, the post precipitation must be small. The action of iron sulfide on aging is different from the others in that the amount of barium ion retained is decreased. Since the amount of barium ion lost after aging (Table II) is the same as when it is added after precipitation (Table I), no post precipitation takes place. It is interesting to note the absence of post precipitation with hydrous ferric oxide.<sup>1c</sup>

### Summary

1. No sulfate ion is formed when the sulfides of the ammonium sulfide group are precipitated.
2. The loss of barium ion when the sulfides form is probably due partly to surface adsorption.
3. As the concentration of ammonium ion is increased, the loss of barium ion is decreased, but some is still lost in a solution saturated with ammonium chloride.
4. The loss of barium ion by occlusion when the sulfides form is small.
5. Postprecipitation causes a large loss of barium ion in the case of nickel, cobalt and manganese sulfides, a small loss with zinc sulfide, and none with iron sulfide.

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