

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

## A Separation of Zinc from Cobalt Based on a New Method for Reducing Post-Precipitation<sup>1</sup>

BY JOHN R. CALDWELL AND HARVEY V. MOYER

At the present time there is no method described in the literature that will give a quantitative separation of zinc sulfide from cobalt in one precipitation. The zinc sulfide always carries down an appreciable quantity of cobalt, and several reprecipitations must be made. Our observations, as well as those of Jeffreys and Swift,<sup>2</sup> indicate that this contamination has a mechanism similar to that described by Kolthoff for the post-precipitation of zinc on copper sulfide.<sup>3</sup>

Recent work published by us has shown that the presence of certain hydrophilic colloids and of some organic compounds exerts a profound influence upon the physical nature of precipitates.<sup>4,5,6</sup> It seemed probable that this principle could be used to reduce post-precipitation and co-precipitation in standard sulfide precipitations.

When zinc sulfide is contaminated with cobalt it is colored green, and the depth of color indicates approximately the relative amount of cobalt carried down.

Two general classes of material were investigated: (a) protective colloids such as agar-agar, gum arabic, egg albumin, etc., were used with the possibility that they might be preferentially adsorbed in place of the hydrogen sulfide and thus reduce the concentration of hydrogen sulfide at the surface of the zinc sulfide particles; (b) organic compounds capable of reacting with hydrogen sulfide were investigated with the expectation that if they were absorbed on the precipitate they might reduce the concentration of hydrogen sulfide below the precipitation value. Among the compounds used for this purpose were alcohols, ketones, aldehydes, nitro compounds, amines, aromatic nitro acids, unsaturated compounds and others.

### Materials

**Standard Zinc Sulfate Solution.**—The preparation of this solution was described in an earlier paper.<sup>6</sup> It was equivalent to 0.3160 g. of zinc oxide per 50 ml.

(1) Presented before the Division of Physical and Inorganic Chemistry at the 89th meeting of the American Chemical Society, New York City, April 22 to 26, 1935.

(2) Jeffreys and Swift, *THIS JOURNAL*, **54**, 3219 (1932).

(3) Kolthoff, *J. Phys. Chem.*, **36**, 549 (1932).

(4) Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(5) Caldwell, *THIS JOURNAL*, **57**, 96 (1935).

(6) Caldwell and Moyer, *ibid.*, **57**, 2372 (1935).

**Cobalt Sulfate.**—A c. p. grade was dissolved and filtered before use. It contained no zinc.

**Organic Compounds, Gums, Colloids, etc.**—A large number of organic compounds and hydrophilic colloids were used in the investigation. No attempt was made to secure these in a purified condition except in those cases discussed in detail below.

### Experimental Work

The substance to be tested was added to 300 ml. of solution containing 0.25 g. of zinc, 0.50 g. of cobalt and 6 to 8 g. of ammonium sulfate. Hydrogen sulfide was passed in for thirty minutes at room temperature, the precipitate flocculated by gelatin,<sup>6</sup> and filtered off. The cobalt content was then determined by comparison with known standards. The amount of cobalt in the standards had been determined colorimetrically by dissolving a precipitate of the same color in hydrochloric acid, and comparing with known amounts of cobalt chloride dissolved under the same conditions. This method was suitable for quantities of cobalt ranging from 0.1 to about 20 mg.

It was found that certain aldehydes would greatly reduce the amount of cobalt carried down. The aldehydes tested were benzaldehyde, cinnamic aldehyde, propionaldehyde, paraldehyde, acetaldehyde, furfural, heptaldehyde, isoamyl aldehyde, *m*-nitrobenzaldehyde, anisaldehyde, crotonaldehyde, chloral, piperonal, paraformaldehyde, glucose, butyraldehyde, formaldehyde and acrolein. Some of the aldehydes were very effective in preventing post-precipitation of cobalt, but they formed troublesome resins which interfered with filtration, or in some cases they prevented complete precipitation of the zinc. It was found that acrolein was best suited for the purpose. It was very effective in small concentrations, did not form a resin readily, and allowed complete precipitation of the zinc.

Freshly distilled acrolein was used for some of the quantitative determinations, but it was found that the liquid part of an old, partly polymerized product was just as effective. For convenience in handling, an aqueous solution containing 4 ml. of acrolein per 100 ml. of water was prepared. About 10 mg. of hydroquinone and 1 drop of concentrated hydrochloric acid were added per 100 ml. of solution to inhibit polymerization. This solution retained its activity for several weeks.

**Quantitative Procedure.**—The quantitative procedure adopted for precipitation of zinc sulfide in the presence of cobalt is but slightly different from conventional methods. The pH of a chloride-free solution containing 0.25 g. of zinc and cobalt up to 0.5 g. is adjusted until the hydroxides just remain in solution, then 6 to 8 g. of ammonium sulfate is added. The total volume is brought to 250 to 300 ml., and 0.2 ml. of acrolein is added. A rapid stream of hydrogen sulfide is passed in at room temperature for thirty minutes. Five to 10 ml. of a 0.02% gelatin solution is added<sup>6</sup> and the precipitate is filtered off after fifteen to

twenty minutes' standing. Cold distilled water is used to transfer and wash the precipitate. In some cases, the filtrate develops a faint white turbidity after standing. This is due to the formation of a small quantity of resinous acrolein-hydrogen sulfide reaction product. If the filtrate is to be used for further analysis, it is strongly acidified and boiled down to about one-third of its original volume. This treatment will drive out most of the acrolein, and if any still remains, it will appear as small yellow flakes which are readily filtered off.

**Quantitative Experiments.**—Solutions containing 50 ml. of standard zinc solution, 0.5 g. of cobalt and 6 to 8 g. of ammonium sulfate were precipitated according to the procedure outlined above. When no acrolein was present, 6 to 10 mg. of cobalt was carried down. When 0.2 ml. of acrolein was added before precipitation, the precipitate contained from 0.2 to 0.4 mg. of cobalt. Four determinations using acrolein yielded weights of zinc oxide that deviated by +0.6,  $\pm$ 0.0, +0.1 and +0.3 mg. from the standard value of 0.3160 g. If more than 0.3 ml. of acrolein was used for 0.25 g. of zinc, there was some resin formation and filtration was retarded.

Kolthoff<sup>3</sup> showed that an increase in temperature caused an increase in the amount of zinc post-precipitated with copper sulfide. We found the same general rule to hold with cobalt and zinc. Acrolein proved to be very effective in preventing post-precipitation in hot solution. Solutions having the composition described above were heated for thirty minutes on a boiling water-bath after precipitation. When 0.20 ml. of acrolein was present, the precipitates contained 0.4 to 0.5 mg. of cobalt. In controls containing no acrolein, more than 30 mg. of cobalt was carried down.

If the solution containing zinc and cobalt is first heated to boiling, and hydrogen sulfide then passed in, the effect of acrolein is not so pronounced, and several milligrams of cobalt is carried down. This may be due to the possibility that acrolein is not so readily adsorbed from hot solution.

**Precipitation in Chloroacetic Acid-Sodium Acetate Buffer.**—For procedures where it is undesirable to have sulfates in the solution, Mayr<sup>7</sup> has proposed the use of a chloroacetic acid-sodium acetate buffer. He reported satisfactory separations from all metals but cobalt. Good

separations were obtained with the use of acrolein, when precipitation was carried out at room temperature. The results are summarized in Table I.

From the table, it is evident that this procedure gives satisfactory separations from cobalt, and from mixtures of iron and cobalt.

**Theoretical Discussion.**—Although a number of aldehydes were effective in reducing post-precipitation, there seemed to be a high degree of specificity in the case of acrolein that made it far superior to all others tried. A probable explanation of the effect may be based on Kolthoff's theory of post-precipitation. He showed that certain organic compounds containing sulfur were adsorbed by cupric sulfide precipitates and reduced the concentration of hydrogen sulfide at the surface. The action of aldehydes in general, and of acrolein in particular, apparently goes one step farther. They not only are readily adsorbed by the sulfide precipitate, but they also react rapidly with the hydrogen sulfide on the surface and reduce its concentration below the precipitation value. A survey of the organic literature shows that in general aldehydes will react with hydrogen sulfide under the above conditions to give various types of polymerized thioaldehydes.<sup>8,9,10</sup>

Microscopic examination of the precipitate shows that a distinct alteration in the nature of the surface has taken place. The reaction is apparently confined mainly to the surface of the particles, because there is very little decrease in hydrogen sulfide concentration in the solution itself.

It is planned to continue this study as applied to the post-precipitation of zinc on copper sulfide.

#### Acknowledgment

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#### Summary

If zinc sulfide is precipitated in the presence of small concentrations of certain aldehydes, particularly acrolein, the amount of cobalt carried down

TABLE I  
PRECIPITATION IN SOLUTION BUFFERED WITH CHLOROACETIC ACID-SODIUM ACETATE

Total volume 250 ml. containing 15 ml. 2 *N* monochloroacetic acid, 15 ml. of 1 *N* sodium acetate, and 0.2 ml. of acrolein. Zinc equivalent to 0.3160 g. of ZnO. Precipitate flocculated by gelatin.

Other metal present in solution, g.	Wt. other metal found in ppt., mg.	Ignited ppt., g.	Dev. from std. soln. value, g.
0.25 Fe } .25 Co }	a	0.3159	-0.0001
.25 Fe } .25 Co }	a	.3158	- .0002
.50 Co	0.3	.3162	+ .0002
.50 Co	.3	.3161	+ .0001

<sup>a</sup> Not determined.

(7) Mayr, *Z. anal. Chem.*, **96**, 273 (1934).

(8) Klinge, *Ber.*, **9**, 1893 (1876).

(9) Baumann, *ibid.*, **22**, 1035, 2605 (1889).

(10) Wörner, *ibid.*, **29**, 139 (1896).

is greatly reduced. This makes it possible to separate zinc and cobalt by one precipitation. Experimental evidence indicates that acrolein reacts

with hydrogen sulfide on the surface of the zinc sulfide particles, thereby reducing post-precipitation.

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## The Accuracy of the Titration of Thiocyanate with Mercuric Mercury

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In a previous paper<sup>1</sup> it was shown that in the direct and the reverse titration of silver with thiocyanate nearly theoretical results are obtained, slight deviations being found as a result of side reactions occurring during the reaction of the silver and thiocyanate ions. It was thought of interest to test the accuracy of the titration of mercuric mercury with thiocyanate and the reverse titration, especially since it had been shown that the end-point could be determined with great precision. The titrations were made potentiometrically and also with ferric iron as indicator.

### Materials and Apparatus

Pure potassium thiocyanate prepared as described in a previous paper<sup>1</sup> was used.

**Mercury.**—The metal was purified in the usual manner by bubbling hot air through it for several hours, followed by washing with dilute nitric acid and distillation in vacuum.

**Mercuric Thiocyanate.**—The salt was precipitated from a dilute potassium thiocyanate solution by adding a slight excess of mercuric nitrate solution. The crystalline precipitate was washed thoroughly with water, and was then recrystallized from a large volume of hot water.

**Mercury Electrode.**—The electrode shown in Fig. 1 was specially designed for this work, the electrode mercury being contained in the conical cup. Electrical connection between the mercury cup and the mercury column in the stem was made by means of a platinum wire, sealed solidly in the neck connecting the cup and stem. The cup had a diameter of 1 cm. at the top and was filled with pure mercury so that the level of the latter was slightly above the rim of the cup. The stem was filled with ordinary mercury into which the copper wire potentiometer lead dipped.

This electrode was much more convenient than the conventional type, prepared by electrodeposition of mercury on a platinum electrode, and it eliminates the trouble of frequent replating necessary with the latter type.

**Standard Solutions.**—Standard stock solutions of potassium thiocyanate were prepared by weight according to the technique already described.<sup>1</sup> Standard mercuric nitrate solutions were prepared by dissolving carefully weighed samples (corrected to vacuum) of the pure metal in a moderate excess of 6 *N* nitric acid, boiling to remove oxides

of nitrogen, and diluting to a known weight. This solution was *ca.* 0.4 *N* (0.2 molar) by weight, and was *ca.* 0.02 *N* in free nitric acid. An exactly 0.05 *N* solution, for the finish of the titrations, was prepared by dilution of a weighed portion of the stock mercuric nitrate solution in a calibrated flask.

The total operative error involved in the preparation of the standard stock solutions (weighing materials and solutions) was probably less than 0.005%. The solutions were stored in the all-glass storage flasks previously described.<sup>1</sup>

### Procedure and Results of the Titrations

The general procedure of the titrations was as follows. A suitable portion of one of the stock solutions (*ca.* 50 g. of the potassium thiocyanate solution or 25 g. of the mercuric nitrate solution) was weighed into a 250-cc. beaker from a weight buret and diluted to 100-125 cc., with addition of sufficient nitric acid to make its concentration 0.1 *N* at the end of the titration. The mercury electrode, stirrer and salt bridge were then placed in the solution and the titrating solution was added from a weight buret with thorough stirring, until the measured e. m. f. indicated that either a slight excess or a slight deficiency had been added. The titration was then finished with the appropriate dilute solution from a calibrated 5-cc. microburet. The end-point was located in the usual way from the maximum in  $\Delta E/\Delta V$ . The final volume at the end of the titration was about 200 cc.

Titrations were made both at room temperature (*ca.* 23°) and at 0°, the titration beaker being placed in a jar of cracked ice for the latter titrations. Titration at 0° is preferable to titration at room temperature because the maximum in  $\Delta E/\Delta V$  at the end-point is much more pronounced (change in solubility and dissociation with temperature). This is illustrated in Fig. 2, in which the data, in the region of the equivalence point, have been plotted for two typical titrations at 23 and at 0°.

Steady e. m. f. readings are obtained very quickly throughout the entire course of the titration, which is a marked advantage of the thiocyanate-mercury titration over the thiocyanate-silver titration.

The results obtained in ten titrations, given in Table I, have been expressed in terms of the ef-



Fig. 1.—Mercury electrode for potentiometric titrations.

(1) I. M. Kolthoff and J. J. Lingane, *THIS JOURNAL*, **57**, 2126 (1935).