

but the principal source of error is in the removal of excess peroxide without decomposing the cobalt compound.

6. Cobalt in alloy steels was determined volumetrically after separation by phenyl-thiohydantoic acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SEPARATION OF COPPER BY MEANS OF PHENYL-THIOHYDANTOIC ACID¹

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During the course of an investigation on the separation of cobalt by means of phenyl-thiohydantoic acid² it was found that in a solution slightly acid with acetic acid, copper, lead, mercury, cadmium, bismuth and antimony are quantitatively precipitated by this reagent, while tin, arsenic and the metals not in the hydrogen sulfide group are not precipitated under these conditions. The bismuth and antimony compounds are soluble in alcohol. The present paper gives the details of the separation of copper by this means.

When pure, the precipitate is bright yellow, but it decomposes so readily to form sulfide that it is usually a dirty yellow. It is, therefore, impossible to weigh the copper in this form. When ignited to oxide, the latter contained sufficient sulfate to cause an error varying from +0.1 to +0.6 mg. It was found desirable, therefore, to dissolve this oxide, preferably by fusion with potassium pyrosulfate, and to determine the copper by any of the well-known methods.

Procedure

The solution is neutralized with ammonia and 5 cc. of glacial acetic acid added. If metals precipitated by ammonia are present, 7 g. of citric acid is first added for every gram of metal. To the boiling solution, 300–400 cc. in volume, is added 0.5 g. of phenyl-thiohydantoic acid dissolved in a little hot water, then dil. ammonium hydroxide until a yellow precipitate just begins to form. It is well at this point to discontinue the addition of ammonia and to boil the solution for a few minutes. If the copper is all precipitated, the yellow precipitate separates at the top leaving a clear solution. If this does not occur, more aqueous ammonia should be added; too much causes appreciable solubility of the precipitate. It also turns brown from the formation of sulfide. Precipitation is complete at once. The solution is filtered hot and the precipitate washed with hot water.

¹ From a dissertation presented by Dorothy Hall in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² THIS JOURNAL, 44, 2219 (1922).

It is ignited to oxide, fused with potassium pyrosulfate, dissolved in water and the copper determined electrolytically or volumetrically. If preferred, the oxide may be dissolved in hydrochloric acid. This separation is best adapted for amounts of copper less than 0.1 g.

As in the case of cobalt, the separation from iron was found to be the most difficult; consequently this is the only one which was studied in detail. In the other cases it was simply shown that the copper was completely precipitated and that no trace of other metals was carried down. If the amount of reagent was doubled a much greater amount of iron was carried down. Samples of an imported pure electrolytic copper were weighed out and dissolved in nitric acid; 1 g. of iron was added as ferric alum, and the copper precipitated as described above, after which it was determined electrolytically. The results are shown in the following table. In Expts. 1-5, 1 g. of reagent was added; in the others, 0.5 g.

Expt.	Cu taken G.	Cu found G.	Error Mg.	Fe in ppt. Mg.
1	0.1051	0.1050	-0.1	8.4
2	0.0676	0.0676	0	6.3
3	0.0773	0.0776	+0.3	4.3
4	0.0828	0.0828	0	6.3
5	0.0603 ^a	0.0602	-0.1	0.6
6	0.0625	0.0628	+0.3	0.4
7	0.0590	0.0590	0	0.1
8	0.0603	0.0605	+0.2	0.4
9	0.0529	0.0525	-0.4	0.1

^a Pptd. in 50% alcoholic solution.

Summary

1. Copper, lead, mercury, cadmium, bismuth and antimony are quantitatively precipitated by phenyl-thiohydantoic acid from a solution slightly acid with acetic acid.
2. Details are given for the separation of copper from the metals of the iron and zinc groups, with quantitative results for the separation from iron.
3. This method is especially adapted for small amounts of copper.

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