THE REMOVAL OF PHOSPHATE BY ZINC OXIDE

HARRIETT BERTOGLIO, MARY LEMON, and OLLIDENE WEAVER, with
W. F. BAILEY
MacMurray College, Jacksonville

The qualitative analysis for the alkaline earth metals requires the prior removal of phosphate ions, which is usually done during the course of the analysis of the ammonium sulfide precipitate. The methods most commonly used are the tin method, whereby the phosphate is removed in nitric acid solution by absorption on beta stannic acid formed from metallic tin, and the better known basic acetate method.

Treadwell and Hall[1] mention that in special cases, zinc oxide may be used, and Lundell and Hoffman[2] list zinc oxide as a means of complete precipitation of phosphorus. A study of the use of zinc oxide for the removal of phosphate in routine qualitative analysis is presented herewith.

Experimental

Since the basic acetate removal of phosphate depends on the regulation of the pH of the solution to the point where ferric phosphate will precipitate without the formation of alkaline earth phosphates, measurements were made to determine the pH of acidic solutions to which zinc oxide had been added. Tenth normal hydrochloric acid was treated with zinc oxide until, after heating and stirring, some solid remained undissolved. The solutions were then cooled and the pH measured electrometrically, using a quinhydrone electrode and a tenth normal calomel reference electrode. The zinc oxide used was Merck's Reagent Grade, both wet and dry process. The results fell between 5.4 and 6.0, values which should assure the quantitative precipitation of ferric phosphate.

Qualitative tests were then made in which solutions of ferric nitrate and the nitrates of the different alkaline earths were mixed with amounts of disodium phosphate somewhat less than the ferric ion, together with just sufficient nitric acid to dissolve the precipitate thus formed. A slight excess of zinc oxide was then added and the mixture heated for several minutes on a water bath. It was then centrifuged and the centrifugate tested for both iron and phosphate and for whichever alkaline earth had been used, after removal of zinc by ammonia and hydrogen sulfide. In all cases, tests for both iron and phosphate were negative and the test for the alkaline earth was positive.

A series of quantitative estimations was then made. Standard solutions were made up of disodium phosphate and the nitrates of ferric iron, cobalt, nickel, barium, strontium, calcium, and magnesium. In standardizing these solutions, cobalt and nickel were determined by elec-

[1] Treadwell and Hall, Analytical chemistry: New York, John Wiley and Sons, vol. I, 5th eng. ed., p. 474.
[2] Lundell and Hoffman, Outlines of methods of chemical analysis: John Wiley and Sons, New York, 1938, p. 90.

TABLE 1.

	Cobalt	Nickel	Barium	Strontium	Calcium	Magnesium
Grams						
Taken.....	0.189	0.176	0.180	0.196	0.196	0.129
Found.....	0.169	0.147	0.156	0.185	0.167	0.119

trometric precipitation, barium and strontium as sulfates, magnesium as the 8-hydroxyquinolate, and calcium as carbonate after precipitation as the oxalate.

Solutions of approximately 40 ml. containing about 0.09 g. of iron and slightly less sodium phosphate together with one of the other nitrates, were treated with just enough nitric acid to dissolve any precipitate formed. About 2 grams of zinc oxide was then added and the mixture heated to boiling and kept hot for five minutes. It was then filtered and the precipitate washed twice with small amounts of hot water. The filtrate was then made alkaline with ammonia and saturated with hydrogen sulfide to precipitate zinc together with cobalt or nickel if these were present. Colbalt and nickel were determined by electrometric precipitation after dissolving the sulfide precipitate in nitric acid, while the alkaline earth elements were determined in the filtrate, using the same methods as were used in standardizing the solutions. In all cases at least two samples containing the same metal were run. Since the investigation was being made to determine the suitability of zinc oxide for use in qualitative analysis, no attempt was made to recover the metallic ion that may have been carried down in the rather voluminous precipitate of ferric phosphate and ferric hydroxide. The results are summarized in table 1.

A rather considerable number of solutions containing either cobalt or nickel together with phosphate and at least one alkaline earth metal were analyzed for the metallic elements, removing the phosphate by means of zinc oxide. The methods for the detection of the cations were those given in *Elementary Qualitative Analysis* by Reedy, since that is the text used in our course in Qualitative Analysis. An exception was made in the detection of cobalt, where the formation of the blue cobalt tetracyanato-mercurate was used. This reaction has been studied by V. J. Cuvelier[3]. Although the compound itself is not of sufficient insolubility to be an extremely sensitive means of detecting cobalt, if the similar white zinc salt is precipitated, it carries down and is colored blue by extremely small amounts of cobalt. Since after the removal of phosphate by zinc oxide, zinc ion is present, it was felt that this would be the best means of detecting cobalt. However, since the presence of nickel makes the detection of cobalt less sensitive, as does dimethyl glyoxime, nickel should first be removed by dimethyl glyoxime, followed by evaporation

[3] V. J. Cuvelier: Z. Anal. Chem. 99, 15, 1934; 102, 16, 1935.

with nitric acid to destroy the excess of dimethyl glyoxime.

The following is the recommended procedure: On a small amount of the nitric acid filtrate remaining after the removal of manganese by potassium chlorate, make a test for iron by means of potassium ferrocyanide. If iron is not present, add to the remainder of the solution sufficient ferric chloride to cause a distinct yellow color. Then add sufficient ammonia to cause the formation of a slight permanent precipitate and then just enough nitric acid to redissolve this precipitate. Then add zinc oxide and heat for several minutes on the water bath, with stirring. The amount of zinc oxide should be sufficient so that some may be seen at the bottom of the container. If ferric hydroxide does not form, add more ferric chloride. Filter, or centrifuge, and after washing with hot water, discard the precipitate. Add sufficient ammonia to make the filtrate alkaline to litmus and if a precipitate forms, filter it out and discard it. Then saturate the solution with hydrogen sulfide, filtering or centrifuging out the precipitate which is examined for cobalt and nickel and reserve the solution for examination for the alkaline earths.

Dissolve the hydrogen sulfide precipitate in hydrochloric acid plus a little nitric acid, filtering out and discarding any sulfur. Test the resulting solution for nickel by making alkaline with ammonia and adding dimethyl glyoxime. When nickel is present, it should be completely removed in order to make the detection of cobalt more sensitive. For this purpose, the sodium salt of dimethyl glyoxime offers the advantage of being more soluble. Filter out and discard the red precipitate. To remove the excess of dimethyl glyoxime, acidify the solution with nitric acid and evaporate to dryness. Moisten the residue with nitric acid and again evaporate to dryness. Dissolve the residue in water after heating with a few drops of dilute hydrochloric acid, filtering out and discarding any residue. Then test the solution for cobalt by the addition of potassium tetrathiocyanato mercurate, made by mixing stoichiometric quantities of potassium thiocyanate and mercuric chloride. In the absence of cobalt, a white precipitate of the zinc salt should form. If cobalt is present, the precipitate will be blue, the depth of color varying with the proportion of cobalt.

The solution reserved for the alkaline earths is then examined for them by the usual methods, after removing ammonium salts with nitric acid.

In the development of the process, several senior students analyzed a considerable number of solutions for the ammonium sulfide group and the alkaline earths, without error. For the past two years, the method has been used in our regular course in qualitative analysis. The results have not been uniformly correct, but they do show a distinct improvement over those obtained previously with the basic acetate method, both in accuracy and saving of time.