INVESTIGATION WITH THE AID OF LABELED ATOMS OF THE CONDITIONS
REQUIRED FOR THE SEPARATION OF ZINC AND COBALT FROM
ALUMINUM AND IRON

Yu. V. Morachevsky and Z. S. Bashun

The separation of tervalent ions from bivalent ions is frequently carried out in the complete analysis of
minerals, rocks, and many industrial products. Many of the methods of separation are based on the precipitation
under various pH conditions, of hydroxides and basic salts of the elements to be separated. This principle lies
at the basis of the precipitation of hydroxides and basic salts of ter-and quadri-valent ions from the buffer
solutions ammonia + ammonium salt (the widely practiced precipitation with ammonia) and ammonium acetate
+ acetic acid (the so-called "acetate hydrolysis" method), and it lies also at the basis of precipitation with weak
organic bases, etc.

The conditions required for maximum completeness of separation have frequently attracted the attention
of investigators. However, the detailed elucidation of the effect of individual factors on completeness of
separation and the complicating phenomenon of coprecipitation was rendered difficult by the complexity and
insufficient sensitivity of methods of determining the distribution of the particular ion between precipitate and
solution.

There are wide possibilities for the application of radioactive isotopes to the accurate determination of the
behavior of an ion in various analytical separations. In our opinion, one of the urgent tasks of modern analytical
chemistry is the detailed study, with the aid of labeled atoms, of the methods of ion separation used in
analytical practice with the object of revealing sources of error and methods of avoiding error. Work in this
direction has already begun [1,2].

In the present paper we give the results of an investigation of three methods of separating aluminum and
iron from zinc and cobalt: 1) precipitation of hydroxides of tervalent metals with ammonia; 2) so-called
"acetate hydrolysis"; and 3) precipitation of aluminum and iron with pyridine. These particular bivalent ions
were selected because conditions for their separation have received very little investigation.

The precipitation of the hydroxides of aluminum, iron, and titanium with ammonia in order to separate
these elements from manganese, calcium, and magnesium is extensively used in the analysis of silicates. The
conditions for separation were studied very fully by Blum [3], who recommended precipitation from hot solutions
containing a sufficient amount of ammonium salts, the pH of the solution being maintained at 6-6.5 with the
aid of Methyl red. The conditions recommended by Blum for the precipitation of aluminum and iron hydroxides
have been accepted by most authors of later publications. Hillebrand and Lundell [4] also recommend the
precipitation conditions proposed by Blum, though they point out that complete separation of aluminum and
iron from zinc, cobalt, and copper is not attained even when the precipitate of hydroxides is reprecipitated ;
they cite the results of Lundell and Knowles [5], which characterize the degree of entrainment of various bivalent
ions by precipitates of aluminum hydroxide formed under Blum's conditions.

The method of so-called "acetate hydrolysis" consists in boiling a very dilute ammonium acetate + acetic
acid buffer solution containing tervalent iron, aluminum, and titanium, which are precipitated as sparingly
soluble basic acetates. As precipitation occurs at relatively low pH (5.2-5.6) [6], it may be expected that,
after reprecipitation, the precipitate will not contain bivalent ions, including those in which we are interested,
zinc and cobalt. This method is often recommended for the separation of iron and aluminum from bivalent ions; its main defect is incomplete precipitation of aluminum, it being generally recommended that its precipitation be completed in the filtrates after the separation of the main precipitate, for which purpose the filtrates are evaporated down to small bulk and their pH is increased somewhat by addition of ammonia [7]. Lassieur [8] considers that complete precipitation of aluminum as basic acetate is attained at pH not less than 5.3.

The use of pyridine for the separation of tervalent ions from bivalent is considered in a series of papers by Ostroumov and coworkers [9-12]. Being a weak base, pyridine precipitates aluminum and ferric hydroxides, whereas it forms soluble complex compounds with several bivalent ions. In order to maintain zinc in solution it has been proposed that a large amount of ammonium chloride be added.

EXPERIMENTAL

1. Behavior of Zinc and Cobalt in the Precipitation of Aluminum and Ferric Hydroxides with Ammonia

A definite amount of the radioactive isotope of zinc or cobalt (Zn⁶⁵ or Co⁶⁰) was introduced into a solution containing known amounts of aluminum or iron and zinc or cobalt in the form of chlorides. The original solution, prepared in this way, was always 100 ml in volume. The solution was heated to the boil, and aluminum or ferric hydroxide was precipitated with ammonia. After ten minutes the hot solution was filtered and the residue was washed with 2% ammonium nitrate solution; the main filtrate and washings were collected separately. The volume of the washings, like that of the original solution, was 100 ml. Activity measurements were made on the filtrate and washings, and the pH of the main filtrate was determined - generally with a quinhydrone electrode, and in control experiments with a hydrogen electrode. The precipitate of hydroxide was dissolved in dilute hydrochloric acid, and aluminum (or ferric) hydroxide was reprecipitated under the same conditions as in the first precipitation. The filtrate and washings were collected separately, each was made up to 100 ml, and their activities were measured. The reprecipitated material was redissolved and its activity was measured.

Thus, activity measurements were taken only on solutions. For this purpose the solutions were placed in glass vessels having two walls of thin glass; 20 ml of solution was always taken. The counter tube was fixed vertically, and the vessel was placed on it. Before each measurement the background of the apparatus and vessel (filled with water) was checked; it was fairly great, but stable, varying between 38 and 41 impulses per minute. In the measurement of the activity of the solutions under investigation, counts were taken over 5-15 minutes, depending on the activity; in the case of very low activity, the count was continued until the total number of impulses registered reached 500. A correction for background was always made to the results of the count. The procedure is outlined schematically on the following page.

Separation of Zinc from Aluminum. The first series of experiments had the object of determining the effect of the pH of the solution on the coprecipitation of zinc with aluminum hydroxide. The contents of aluminum and zinc were not varied. The results are given in Table 1.

It will be seen from Table 1 that complete separation of aluminum and zinc under the selected conditions (identical with those recommended by Blum) is attained only at pH values lying within very narrow limits, 5.5-5.8. With rise in pH to about 7, the zinc content of the reprecipitated precipitate increases; with further rise in pH the amount of zinc carried down with the precipitate begins to diminish owing to partial formation of a zinc ammine; at pH 9.4 (considerable excess of ammonia) the precipitate contains only 1.9% of the whole of the zinc. Further rise in pH is made difficult by the buffering action of the ammonium salt, but it is of no practical interest since the precipitation of aluminum was found to be incomplete under these conditions.

Ammonium chloride, apart from having a buffer action and improving conditions for coagulation of the hydroxide, reduces coprecipitation of zinc due to exchange adsorption. Special experiments showed that reduction of the concentration of ammonium salt without change in other conditions results in increase in the entrainment of zinc by the precipitate; on the other hand, increase in the concentration of ammonium chloride beyond 5% had no effect on the results of the experiments.