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Organic Reagents[1] in Qualitative Analysis. I. The Separation of Iron, Chromium and Aluminum

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In the usual methods of analysis of the ammonium sulfide group a mixture of sodium hydroxide and sodium peroxide is employed to separate the iron and aluminum groups.[2,3] It is a well known fact that these reagents, especially the former, due to its action on glass, introduce small amounts of aluminum and silica into the solution.[4,5] In the final precipitation of aluminum ion by ammonium hydroxide any silica originally present will also be precipitated as silicic acid. This precipitate may be mistaken for aluminum hydroxide, though the use of aluminon will overcome this possible error.[6] However, it would be preferable to separate and detect aluminum ion without the use of sodium hydroxide and sodium peroxide or at least before they are added.

The problem would be simplified considerably if it were possible to separate the trivalent from the divalent metallic ions. Ammonium hydroxide in the presence of ammonium salts has been shown to be unreliable[7] even when the *P*H of the solution has been controlled.[8] Recently the separation of ferric ion from the divalent metallic ions was reported by using hexamethylenetetramine which, it is stated, acts as a very weak base in acid solution and precipitates ferric hydroxide.[9] The authors claim that from a study of the *P*H's at which chromic hydroxide and the hydroxides of the divalent metallic ions form, it would be impossible to make a separation. However, experimentation showed that in separate boiling solutions of each metallic ion containing ammonium salts only the trivalent ions are

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(1) The organic reagents are made by the Eastman Kodak Co., Rochester, N. Y.

(2) Noyes, "Qualitative Chemical Analysis," 9th Ed., The Macmillan Co., N. Y., 1927, p. 95.

(3) Curtman, "Qualitative Chemical Analysis," The Macmillan Co., N. Y., 1931, p. 323.

(4) Ref. (1), p. 99, Note 5.

(5) Ref. (2), p. 327, Note 21.

(6) Hammett and Sottery, THIS JOURNAL, **47**, 142 (1925).

(7) Noyes, Bray and Spear, *ibid.*, **30**, 482, Notes 2, 3, 4, 5, 495–499 (1908); W. D. Treadwell, *Schweiz. Chem.-Ztg.*, **2**, 59 (1918).

(8) Swift and Barton, THIS JOURNAL, **54**, 2219 (1932).

(9) Ray and Chattopadaya, *Z. anorg. allgem. Chem.*, **169**, 99–112 (1928).

precipitated by hexamethylenetetramine. This fact suggested a possible method of separation when the metallic ions are present together. Further work confirmed this possibility.

Experimental

Reactions of the Metallic Ions with Hexamethylenetetramine.—To 100 mg. separately of each of the metallic ions in 10 cc. of solution, excess 10% $(CH_2)_6N_4$ in water solution was added. If precipitation took place the reagent was added until complete and the mixture filtered. To both the filtrates and the solutions in which there was no precipitation, concentrated ammonia was added to distinct alkalinity and then hydrogen sulfide passed in. The experiments were repeated only boiling after the addition of $(CH_2)_6N_4$ and in a third group 1 g. ammonium nitrate was added first. Table I shows the results of these experiments.

TABLE I

REACTIONS OF METALLIC IONS WITH $(CH_2)_6N_4$

Metallic ion	$(CH_2)_6N_4$, precipitation	$(CH_2)_6N_4$ + boiling, precipitation	1 g. NH_4NO_3 + $(CH_2)_6N_4$, precipitation	1 g. NH_4NO_3 + $(CH_2)_6N_4$ + boiling, precipitation
Fe^{+++}	Complete	Complete	Complete	Complete
Al^{+++}	None	Complete	Complete	Complete
Cr^{+++}	None	Complete	None	Complete
Ni^{++}	None	Partial	None	None
Co^{++}	None	Partial	None	None
Mn^{++}	None	Partial	None	None
Zn^{++}	Partial	Complete	None	None
Fe^{++}	Partial	Partial	Partial	Partial

Separation of Trivalent Metallic Ions from Divalent.—To a mixture of 100 mg. of Fe^{++} and 5 mg. of Mn^{++} in a solution of 75 cc. of 0.3 *N* hydrochloric acid containing 1 g. of ammonium nitrate, comparable to the filtrate from the previous group after the hydrogen sulfide has been boiled out, 5 cc. of 3% hydrogen peroxide was added and boiled for five minutes in order to oxidize the Fe^{++} to Fe^{+++}; 10% $(CH_2)_6N_4$ solution was then added to the boiling solution until no more precipitation took place. The filtrate was concentrated to 20 cc. and divided in half. Both solutions were treated with ammonium sulfide, the precipitates filtered and washed. One precipitate was tested for Mn^{++} by the sodium bismuthate method and the other by a sodium carbonate bead and potassium chlorate. Both methods gave positive results. The experiment was repeated using 100 mg. of each of the other trivalent metallic ions separately and 5 mg. of Mn^{++}. Positive tests for Mn^{++} were obtained. Further experiments showed that 1 mg. of Mn^{++} originally in the presence of 100 mg. of each of the trivalent metallic ions together could be detected by the sodium bismuthate method and 2 mg. by the bead test. A solution of 100 mg. of each of the trivalent metallic ions together was carried through the same procedure. The filtrate after the addition of $(CH_2)_6N_4$ yielded no precipitate with ammonium sulfide, showing complete precipitation by $(CH_2)_6N_4$.

The above experiments were repeated using Zn^{++} instead of Mn^{++}. The filtrates from the $(CH_2)_6N_4$ precipitation were evaporated to 10 cc., cooled, filtered if salts crystallized out, and the filtrates tested for Zn^{++} with freshly prepared potassium ferrocyanide solution. The results showed that 1 mg. of Zn^{++} originally in the presence of 100 mg. of each of the trivalent metallic ions together could be detected.

The same experiments were carried out separately with Ni^{++} and Co^{++} and gave similar results, the Ni^{++} being detected with dimethylglyoxime and the Co^{++} by α-nitroso-β-naphthol.

A solution containing 100 mg. each of the trivalent metallic ions, 2 mg. of Mn^{++} and 1 mg. each of the other divalent metallic ions was used in the next experiment. The filtrate from the $(CH_2)_6N_4$ precipitation was analyzed for each divalent metallic ion, positive tests resulting.

Before the procedure could be tried to find out if small amounts of the trivalent metallic ions in the presence of large amounts of the divalent could be separated, an adequate method of detecting the trivalent metallic ions when together was necessary. The method finally developed precipitates Fe^{+++} with cupferron,[10] oxidizes Cr^{+++} to $CrO_4^{=}$ with ammonium persulfate in the presence of silver ion[11,12] and detects Al^{+++} in a weakly acid solution with $(CH_2)_6N_4$. Experiments showed that 1 mg. of each of the trivalent metallic ions together in the presence of 100 mg. of each of the divalent together were effectively separated and detected. Furthermore, it was shown that 1 mg. of each trivalent metallic ion in the presence of 100 mg. of each of the other metallic ions of this group together could be separated and detected.

In order to determine whether or not any Al^{+++} is introduced from the metallic ions of previous groups, a 50-cc. solution containing 100 mg. of each of these metallic ions was made. The silver group was precipitated with Cl^- and filtered, the Cl^- in the filtrate removed by evaporation with HNO_3[13] and after adjustment of the acidity to 0.3 *N* hydrochloric acid completely precipitated with hydrogen sulfide. The filtrate, after removal of the hydrogen sulfide, was concentrated and divided into three portions. One portion was treated with ammonium hydroxide, the second with ammonium sulfide and the third with $(CH_2)_6N_4$ and boiled. No precipitate formed in any case, showing that no Al^{+++} had been introduced.

Summary

1. The reactions of the metallic ions of the ammonium sulfide group with hexamethylenetetramine under varying conditions have been investigated.

2. A separation of the trivalent from the divalent metallic ions, based on these reactions, has been effected.

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[10] Baudisch and King, *J. Ind. Eng. Chem.*, **3**, 629 (1911).

[11] Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900).

[12] Yost, This Journal, **48**, 152 (1926).

[13] Lehrman, *J. Chem. Ed.*, **10**, 50 (1933).