

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Benzoate Method, A New Procedure for the Separation of Iron, Aluminum and Chromium from the other Ions of the Third Group and the Alkaline Earth IonsBY I. M. KOLTHOFF, V. A. STENGER¹ AND B. MOSKOVITZ

Although various methods have been proposed to replace precipitation of aluminum, trivalent iron and chromium by ammonium hydroxide, none has attained great popularity. The ammonia method is tedious, due to the slow filtration and necessity for reprecipitations. The separation of considerable amounts of cobalt, nickel or zinc is unsatisfactory.² W. F. Hillebrand and G. E. F. Lundell³ have discussed the limitations of the basic acetate and succinate methods. In this Laboratory we have had little success with such hydrolytic precipitants as potassium biphthalate, hexamethylenetetramine⁴ and urea⁵ for quantitative separations. Generally, one attains completeness of precipitation of the trivalent metals at the cost of increasing coprecipitation when one increases the amounts of precipitating agents employed.

During the investigation of various reagents, it was noticed that ammonium benzoate distinguishes itself favorably in so far as it allows a complete precipitation of iron, aluminum and chromium at lower *P_H* values and yields precipitates which are more easily filterable than those formed with other agents. These facts gave promise of improving the analytical separations from various divalent cations. Upon addition of ammonium benzoate to ferric or aluminum chloride in weak acetic acid solution, voluminous precipitates are formed at once, but five minutes of gentle boiling are necessary to bring about complete precipitation. With chromic chloride the precipitate does not form until the solution is heated, twenty minutes of boiling being required to complete the coagulation. The precipitates contain considerable benzoic acid, probably in the adsorbed state, and appear to be of variable composition depending upon the *P_H*. At higher *P_H* (5 to 6) they become

more slimy, like hydrous oxides, while addition of excess ammonium hydroxide removes nearly all the benzoic acid.

Precipitates of iron and chromium filter nearly as rapidly as one can pour the suspension over the filter. Aluminum is much slower; nevertheless it requires less than half the time of the ammonia method. In any case, speed of filtration decreases with increasing excess of benzoate or increasing *P_H*. The precipitates are peptized by washing with water; therefore solutions containing benzoate should be used for this purpose.

Materials Used

Aluminum Chloride.—A c. p. product was dissolved in ether and precipitated as the hexahydrate with hydrogen chloride. The crystals were washed with a mixture of pure methanol and ethanol, which dissolved part of the salt but removed practically all of the excess acid as shown by analysis of a stock solution.

Ferric Chloride.—A c. p. product, which according to analysis appeared to be pure, was used without further purification.

The other salts used were c. p. chlorides which did not require further purification for the present purpose.

Reagents

Ammonium Benzoate.—A U. S. P. standard brand used contained 0.05% ash, part of which could be removed by filtering the solution. If the precipitates are to be subsequently ignited, the benzoate should be further purified by recrystallization from dilute ammoniacal solution. In this study solutions containing 100 g. of ammonium benzoate per liter were employed as the precipitant. Growth of a slight mold upon standing can be prevented by addition of 1 mg. of thymol per liter. These solutions had a *P_H* around 6.3 and were quite stable in glass containers.

Wash Solution.—One liter of the solution contained 100 cc. of ammonium benzoate reagent and 20 cc. of glacial acetic acid and had a *P_H* around 3.8. The solution is used hot, as benzoic acid separates at room temperature.

Procedure

A hydrochloric acid solution of the ions, containing the iron in the oxidized state and diluted to about 100 cc., is treated with dilute ammonium hydroxide until the precipitate formed redissolves very slowly upon stirring. One cc. of glacial acetic acid and enough ammonium chloride to make the latter's content at least 1 g. are added, and about 20 cc. of ammonium benzoate reagent is slowly stirred in for every 65 mg. Al, 125 mg. Fe or 125 mg. Cr present. The suspension is heated with stirring until boiling begins and kept at gentle boiling from five

(1) Holder of the J. T. Baker Fellowship for analytical chemistry during the year, 1932-1933, at the University of Minnesota.

(2) G. E. F. Lundell and H. B. Knowles, *THIS JOURNAL*, **45**, 680 (1923).

(3) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, pp. 70-74.

(4) L. Lehrman, E. A. Kabat and H. Weisberg, *THIS JOURNAL*, **55**, 3509 (1933).

(5) See H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Company, New York, 1933, p. 301.

minutes, in the absence of chromium, to twenty minutes if chromium predominates. The mixture is then filtered over coarse paper, 11 cm. paper being suitable for the above amounts of a single metal or proportional amounts of mixtures. The precipitate is washed ten times with hot wash solution. For exact work the filtrate and washings should be evaporated to about 50 cc. for the recovery of incompletely precipitated iron or chromium.

Qualitative Part.—In Table I is shown the behavior of various cations alone when treated according to the standard procedure.

TABLE I

PRECIPITATION OF VARIOUS ELEMENTS BY AMMONIUM BENZOATE IN ACETIC ACID SOLUTION

	Quantitative precipitation Color ppt.		Partial precipitation Color ppt.	No precipitation
Al ⁺⁺⁺	White	U ^{VI}	Yellow ^a	V ^{IV} , V ^V
Cr ⁺⁺⁺	Gray green			Co ⁺⁺ , Ni ⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺
Fe ⁺⁺⁺	Orange tan	Be ⁺⁺	White	Ca ⁺⁺ , Ba ⁺⁺ , Sr ⁺⁺ , Mg ⁺⁺
Ti ⁺⁺⁺⁺	White	Ti ⁺⁺⁺	Brown ^b	K ⁺ , Na ⁺ , NH ₄ ⁺ , Li ⁺
Zr ⁺⁺⁺⁺	White	Pb ⁺⁺	White	Fe ^{++b}
Th ⁺⁺⁺⁺	White	Cu ⁺⁺	Light blue	Cd ⁺⁺
Ce ⁺⁺⁺⁺	Yellow	Sn ⁺⁺	White ^b	Hg ⁺⁺
Bi ⁺⁺⁺	White			Ce ^{+++b}
Sn ⁺⁺⁺⁺	White			

^a Uranyl acetate gives a yellow crystalline precipitate completely soluble in ammonium carbonate.

^b These ions are easily oxidized under experimental conditions, yielding precipitates of the oxidized forms.

The completeness of the precipitation of aluminum, iron and chromium was tested separately by determining the amounts of these metals present in the combined filtrates and washings obtained according to the standard procedure: 0.07 mg. of aluminum, 0.08 mg. of iron and 0.12 mg. of chromium were found, respectively. Solutions containing 0.05 mg. of iron per 100 cc. yield a barely visible precipitate which is easily detected on the filter, whereas 0.15 mg. of aluminum and 0.5 mg. of chromium in 100 cc. give a visible turbidity.

The benzoate procedure can be applied advantageously in ordinary qualitative analysis. The filtrate, after the treatment with hydrogen sulfide in acid solution, is boiled until the excess sulfide is removed; the iron is oxidized, and the solution is further treated according to the standard procedure. Aluminum, iron and chromium are quantitatively precipitated. The precipitate is treated with 1 *N* sodium hydroxide and hydro-

gen peroxide; iron oxide remains insoluble, whereas chromate and aluminum in the filtrate are detected by ordinary methods. The filtrate from the benzoate precipitation, after addition of ammonia and ammonium sulfide, can be further treated according to the common methods of qualitative analysis. The benzoate does not interfere with the precipitation of the alkaline earths. It should be mentioned, however, that part of any phosphate present is in solution after the benzoate treatment. With aluminum and chromium much of the phosphate is found in the filtrate, whereas most of it precipitates with the iron.

Coprecipitation of Zn, Mn, Co, Ni, Ca, Sr, Ba and Mg with Iron, Aluminum and Chromium.—Precipitations of the trivalent metals in the presence of the above divalent cations were made under varying conditions. The amount of coprecipitated cations was usually determined by analysis of the second filtrate obtained after reprecipitation according to the same method. Tests with each metal in amounts of the same order as those coprecipitated using larger quantities showed the reliability of the procedure (see tables). In general this method yielded much more accurate results than a determination of the metal in the first filtrate.

Methods of Analysis.—Since the coprecipitation in general was very small, special methods had to be employed in order to determine the traces of the respective cations. In all cases blanks were run with solutions having about the same composition as the unknowns.

Zinc.—Zinc was determined by precipitating with 8-hydroxyquinoline and weighing or titrating the precipitate. Benzoate does not interfere with this precipitation.

Manganese.—This cation was determined colorimetrically after oxidation with potassium periodate.⁶ Most of the benzoate was removed by filtering the acidified solution and the remainder was eliminated, together with the chloride, by evaporation with sulfuric acid.

Cobalt.—Cobalt was determined colorimetrically by adding 35 cc. of acetone, 5 g. of potassium thiocyanate and 2 cc. of glacial acetic acid and diluting to 100 cc. Addition of fluoride made the iron harmless if the latter happened to be present.⁷ Benzoate does not interfere.

(6) H. H. Willard and L. H. Greathouse, *THIS JOURNAL*, **39**, 2366 (1917).

(7) I. M. Koltzoff, *Mikrochem.*, **8**, 176 (1930); see also E. S. Tomula, *Acta Chem. Fennica*, No. 3-7 (1929).

Nickel.—Nickel was determined gravimetrically or colorimetrically with dimethylglyoxime. In the latter case benzoate had to be removed, whereas the gravimetric determination could be made in the presence of benzoate if digested with reagent for twenty-four hours.

Magnesium.—Magnesium was determined colorimetrically by the titan-yellow method.⁸ Benzoate does not interfere.

Calcium.—Calcium was precipitated as oxalate and the latter titrated.

Barium and Strontium.—These were approximated in the residue after ignition of the filtrate by turbidimetric measurements as sulfate and oxalate, respectively.

TABLE II

COPRECIPITATION OF ZINC					
Trivalent metals taken, mg.	Zn taken, mg.	Benzoate reagent, cc.	Minutes boiled	Zn in ppt., mg.	Zn copptd., %
Al 68.1	180	20	5	1.45	0.80
Al 68.1	36	20	5	0.43	1.19
Al 68.1	1.1	30	10	(<0.15)	<13.6
Cr 165	90	20	20	5.6	6.22
Cr 165	90	30	20	10.1	11.2
Fe 140	90	20	10	0.35	0.39
Fe 140 ^a	202	20	5	.65	.32
Al 27.2	90	20	15	1.0	1.11
Fe 56.1					
Cr 41.3					

^a 2 cc. of glacial acetic acid present.

TABLE III

COPRECIPITATION OF MANGANESE (ADDED AS SULFATE)					
Trivalent metals taken, mg.	Mn taken, mg.	Benzoate reagent, cc.	Minutes boiled	Mn in ppt., mg.	Mn copptd., %
Al 68.1	76.5	20	5	0.07	0.09
Al 68.1	76.5	30	5	.29	.38
Cr 206	76.5	20	15	.75	.98
Fe 140	76.5	20	5	.15	.20
Fe 140	254	30	10	.20	.08
Al 27.2	76.5	20	5	.32	.42
Fe 56.1					
Cr 41.3					

TABLE IV

COPRECIPITATION OF COBALT					
Trivalent metals taken, mg.	Co taken, mg.	Benzoate reagent, cc.	Minutes boiled	Co in ppt., mg.	Co copptd., %
Al 68.1	72.3	20	5	0.27	0.37
Al 68.1	72.3	30	5	.60	.83
Al 68.1	1.0	20	10	.01	1
Cr 165	72.3	20	20	1.33	1.84
Cr 165	72.3	30	20	2.86	3.96
Fe 140	124	30	10	0.10	0.08
Al 27.2	72.3	20	15	.30	.41
Fe 56.1					
Cr 41.3					

(8) I. M. Kolthoff, *Biochem. Z.*, **185**, 344 (1927).

TABLE V

COPRECIPITATION OF NICKEL					
Trivalent metals taken, mg.	Ni taken, mg.	Benzoate reagent, cc.	Minutes boiled	Ni in ppt., mg.	Ni copptd., %
Al 68.1	82.2	20	5	0.28	0.34
Al 68.1	2.24	20	5	0.18	8.0
Cr 206	82.2	20	15	1.85	2.25
Cr 206	2.24	20	15	0.26	11.6
Fe 140	123.5	30	10	<.10	<0.08
Al 27.2	82.2	20	10	.32	.39
Fe 56.1					
Cr 41.3					
Al 27.2	2.24	20	10	.18	8.0
Fe 56.1					
Cr 41.3					

TABLE VI

COPRECIPITATION OF MAGNESIUM					
Trivalent metals taken, mg.	Mg taken, mg.	Benzoate reagent, cc.	Minutes boiled	Mg in ppt., mg.	Mg copptd., %
Al 68.1	60	20	10	<0.05	<0.08
Cr 206	60	20	15	<.05	<.08
Fe 140	60	20	5	.12	.20
Al 27.2	15	20	15	<.02	<.13
Fe 52.1					
Cr 41.3					
Al 27.2 ^a	15	20	15	<.02	<.13
Fe 56.1					
Cr 41.3					

^a In presence of 100 mg. of KH_2PO_4 .

TABLE VII

COPRECIPITATION OF CALCIUM					
Trivalent metals taken, mg.	Ca taken, mg.	Benzoate reagent, cc.	Minutes boiled	Ca in ppt., mg.	Ca copptd., %
Al 68.1 ^a	62	20	5	0.38	0.61
Al 68.1	250	30	5	<0.03	<0.01
Cr 206	100	30	15	1.11	1.11
Cr 206	50	40	15	1.24	2.48
Cr 206	1.0	20	20	0.03	3
Fe 140	100	40	5	.26	0.26
Fe 140 ^a	62	20	5	.51	.82
Al 27.2	100	20	15	.13	.13
Fe 56.1					
Cr 41.3					
Al 27.2	50	30	15	.25	.50
Cr 124					

^a In presence of 50 mg. of KH_2PO_4 .

The results on the coprecipitation of the various metals with iron, aluminum and chromium alone or with mixtures of the latter are given in the following tables, in which about one-third of all data, selected at random, are presented.

The coprecipitation of strontium and barium was of the same order as but always smaller than that of calcium.

Discussion

An inspection of the tables shows that in most cases the coprecipitation is small and one precipitation may yield satisfactory results. If the coprecipitation cannot be neglected, a reprecipitation by dissolving the precipitate in hydrochloric acid and repeating the procedure will give a virtually complete separation.

Quite generally the coprecipitation increases with increasing amounts of benzoate and time of boiling. This may partly explain why the coprecipitation with chromium alone is more serious than with aluminum and iron. Fortunately, those cases in which chromium alone has to be separated from the divalent cations rarely occur. Addition of aluminum or ferric iron reduces the coprecipitation with chromium markedly. None of the trivalent metals volatilize on ignition of the benzoate precipitate. However, phosphate, if present in the original solution, is partly coprecipitated with the trivalent metals and will be present in the ignited residue. In the quantitative analysis of the benzoate precipitate it is preferable to follow a procedure

similar to that described in the qualitative part⁹ of this paper.

After oxidizing in alkaline medium with hydrogen peroxide and removing the excess of the latter by boiling, the iron is filtered off and determined volumetrically. The filtrate is acidified and the aluminum precipitated according to the benzoate method. The chromate in the filtrate is determined volumetrically. The aluminum in the precipitate is determined by precipitation from ammoniacal tartrate solution with 8-hydroxyquinoline.

Summary

The benzoate method gives a simple and rapid procedure for the separation of iron, aluminum and chromium from other cations of the third and fourth groups. In all cases the coprecipitation is much less than that which occurs in the ammonia method, and one precipitation will often suffice in ordinary separations. In more precise analyses a reprecipitation is made. Phosphate is partly precipitated with the trivalent metals.

(9) See also Hillebrand and Lundell, Ref. 3, p. 85.

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The Volumetric Determination of Tin; Use of Potassium Iodate

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Iodine in potassium iodide solution is most generally used in the volumetric determination of stannous tin. Since the iodine-stannous reaction induces the oxygen-stannous reaction, according to Kolthoff,¹ the possible existence of less "inducing" oxidants suitable for determining tin in the presence of oxygen was considered. That iodate might be such an oxidant is indicated from the results obtained by its use in the determination of sulfite,^{2,3} if the lower results found with other oxidants are considered as due principally to the induced sulfite-oxygen reaction. Under the experimental conditions of Bonner and Yost,³ the relative number of equivalents of iodate reduced to iodide by sulfite is slightly but definitely greater than that of triiodide.

The reduction of iodate to iodine monochloride

(1) Kolthoff and Furman, "Volumetric Analysis," 1929, Vol. II, p. 412.

(2) Hendrixson, *THIS JOURNAL*, **47**, 1319 (1925).

(3) Bonner and Yost, *Ind. Eng. Chem.*, **18**, 56 (1926).

via iodine, according to the method of Andrews,⁴ has been applied by Jamieson⁵ to the determination of tin. A high concentration of hydrochloric acid (above 4 *N*) must be maintained in this method. A study of the reduction of iodate to iodide by stannous tin in acid solution has to our knowledge not been reported. The effects of variation in acid concentration, stannous concentration, and order of mixing have been studied.

Reagents

Sodium oxalate, obtained from the United States Bureau of Standards, was the weight basis of the standard solutions (approximately 0.1 *N*) used. The methods of preparation and standardization were as follows: potassium permanganate according to the method of McBride,⁶ sodium thiosulfate (containing 0.2 g. of sodium carbonate per liter) by the Volhard method, under the conditions recommended by Bray and Miller;⁷ potassium iodate

(4) Andrews, *THIS JOURNAL*, **25**, 756 (1903).

(5) Jamieson, *J. Ind. Eng. Chem.*, **8**, 500 (1916).

(6) McBride, *THIS JOURNAL*, **24**, 393 (1912).

(7) Bray and Miller, *ibid.*, **46**, 2209 (1924).