STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS.
I. THE PRECIPITATION BY AMMONIUM HYDROXIDE

BY ERNEST H. SWIFT AND R. C. BARTON

Introduction

During the course of an attempt to develop a system of qualitative analysis for the so-called common elements which would provide more quantitative information than that usually obtained, it became one of the first problems to examine the methods commonly used for the qualitative separation of these elements into groups.   The extensive investigations of Noyes and Bray and their co-workers[1,2,3] have furnished much information as to the qualitative value of many of these separations, with special reference to the detection of very small amounts of one element in the presence of large amounts of the other, but very little information with respect to the completeness of the separation when each element is present in moderate or large amounts.   Although these same separations are used in quantitative methods, surprisingly little systematic information of this nature seems to be collected in texts or reference works; while that in the original literature is widely scattered, gathered under such varying conditions as to be difficult to correlate, and apparently quite incomplete. Therefore it has seemed worth while to present the results of these studies in this series of papers.

The Precipitation by Ammonium Hydroxide.—The precipitation by ammonium hydroxide can well be termed one of the classical analytical separations and, as is stated by Hillebrand and Lundell,[4] "One of the commonest operations the analyst has to perform ..., with the object either of weighing the precipitated compound or of effecting a joint separation of two or more metals from others."   That it may be inadequate even as a qualitative separation in certain cases is shown by the experiments of Noyes and Bray[5] in which, with large amounts of aluminum or ferric iron (100–200 mg.) and with amounts of cobalt, zinc or nickel up to 20 mg., from 75 to 99% of the latter elements were found to be carried down

[1] Noyes and Bray, THIS JOURNAL, **29**, 137 (1907).

[2] Noyes, Bray and Spear, *ibid.*, **30**, 481 (1908).

[3] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927.

[4] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. 69.

[5] Ref. 3, pp. 153–155.

in the precipitate. Noyes, Bray and Spear[6] also state that "a large quantity of zinc may be quantitatively precipitated by ammonium hydroxide when a larger proportion of chromium is present; and manganese will in any case be partially precipitated by that reagent owing to its oxidation by the air." In a careful study of the conditions necessary for securing complete precipitation of aluminum by ammonia, Blum[7] has found that these are attained by carefully neutralizing the solution, using methyl red (or rosolic acid) as indicator, and avoiding an excess of ammonia. Concerning its separation from other elements the following statement is made: "It is well recognized that the separation of aluminum from such elements as zinc, manganese, nickel and cobalt by means of ammonia is unsatisfactory since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminum hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of the manganese occurred so rapidly as to preclude a quantitative separation."

However, Lundell and Knowles[8] in an extensive series of experiments, in which the precipitations were carried out according to the procedure developed by Blum,[7] show that moderate amounts of iron and aluminum can be separated from manganese and nickel quite satisfactorily; under the same conditions considerable amounts of cobalt, copper and zinc were found in the precipitates. It was also found that an excess of ammonia, although apparently improving the separation of aluminum and iron from copper and zinc, made the separation of these two elements from manganese, nickel and cobalt less satisfactory. The striking experiments of Noyes and Bray, cited above, in which a relatively large excess of ammonia was present, seem to confirm this latter observation and to raise considerable question as to whether a more effective separation is obtained by having an excess of ammonia present. This would seem to depend upon whether the bivalent elements remain in solution due to the solubility of their hydroxides (as is most probable with manganese) or due to the formation of the soluble ammonia complexes, and, furthermore, to the relative tendency of these two molecular types to be carried down with the precipitate. The effect of the P_H of the solution upon the adsorbing tendency of the precipitate has also to be considered. In spite of this uncertainty, the proper attention apparently has not been given, in qualitative procedures (or in quantitative methods where the complete precipitation of aluminum is not involved), to the effect of making a careful neutralization or of exactly adjusting the excess of ammonia. It will be shown in the experiments to be presented that the proper control of the excess of am-

[6] Ref. 2, p. 482.

[7] Blum, This Journal, **38**, 1291 (1916).

[8] Lundell and Knowles, ibid., **45**, 676 (1923).

monia is a most important feature in the separations which have been included in the present investigation, and that many of these separations are quite inadequate even for crude qualitative separations unless the neutralization with ammonia is carefully performed.

This study has been restricted mainly to the elements iron, aluminum, chromium, manganese, nickel, cobalt and zinc; however, since in the qualitative analysis of the common elements, the ammonium hydroxide separation is likewise used to separate bismuth from copper and cadmium, a few experiments are shown to indicate the sharpness of these separations. The effect of phosphate has not been included in this paper. It has not seemed worth while to give separate references to all of the previous work dealing with each of the individual separations here studied. In most cases these can be found, with a brief discussion, in the reference work of Rüdisüle.[9]

Experimental Procedure

The separations were carried out according to three general procedures. The first of these, designated Procedure I, was designed to conform to usual qualitative technique, and, except where explained by notes, was as follows.

To a boiling solution containing the elements to be separated and 60 milli-equivalents of hydrochloric acid in a volume of 100–125 ml., 6 normal ammonium hydroxide was slowly added until red litmus paper just turned a distinct blue color. The mixture was then boiled for one to three minutes and filtered; it was kept hot during the filtration. The precipitate was washed with hot water until the washings were colorless or had no perceptible effect on red litmus.

Procedure II, conforming more closely to the procedure outlined by Blum, was as follows.

To a boiling solution, which contained 10 g. of ammonium chloride and 6–12 milli-equivalents of hydrochloric acid in a volume of approximately 250 ml., 6 normal ammonium hydroxide was added dropwise until a color change was noted using methyl red, or in a few cases rosolic acid, as the indicator. Where the color of the solution prevented the use of the internal indicator, litmus test papers were used and the ammonia added until the color of the litmus matched that obtained from a similar solution of ammonium chloride and hydrochloric acid to which ammonium hydroxide had been added until the methyl red (or rosolic acid) color transition occurred. Extreme care was taken in these neutralizations; if the color transition was over-run, the mixture was made acid and the process repeated. The mixture was boiled for one to two minutes and filtered; it was kept hot until the filtration was completed. To expedite filtering and washing two separate filters were used in most cases. The precipitate was washed with a hot 2% solution of ammonium chloride until the washings gave no appreciable precipitate when tested with ammonium sulfide solution.

Procedure II differs from Procedure I in that the solution was diluted to a larger volume, a larger quantity of ammonium chloride was present and extreme care was taken to avoid an excess of ammonium hydroxide.

---

[9] Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Max Drechsel, Bern.

In order to compare more exactly the effect of an excess of ammonium hydroxide the experiments labeled III were performed. These duplicated Procedure II except that after carefully neutralizing with ammonia an excess of 2 ml. of 6 normal solution was added.

In each of the experiments 250 milligrams of one of the elements listed in the first column of the table was precipitated from a solution which also contained 250 milligrams of one of the elements listed at the top of the four major columns. Observations and variations from the procedures outlined above are contained in the notes to the table. The precipitate was then analyzed in order to determine the amount of the soluble element carried down. Limitation of space has made it necessary to omit a detailed description of the methods used in analyzing these precipitates. In every case the precipitate was so treated as to separate the two elements—thus the ferric hydroxide precipitates were dissolved in hydrochloric acid, the concentration of the acid properly adjusted and the iron removed by repeated extraction with ether—or the element carried down was converted into a form in which it could be directly estimated; for example, the manganese in the aluminum precipitate was converted directly into manganese dioxide, or, when very small in amount, oxidized to permanganate. The methods used were checked by blanks and by confirmatory analyses of prepared mixtures. The results of these experiments, showing the amount of co-precipitation in each separation, have been collected in Table I. It is felt that significance should be attached to the general magnitude, rather than the exact value for any individual experiment, as it is impossible to duplicate exactly all the conditions, such as local concentration of the precipitant during precipitation, and as in many cases the results are apparently highly dependent upon such conditions.

TABLE I

THE SEPARATION OF CHROMIUM, ALUMINUM AND IRON FROM MANGANESE, NICKEL, COBALT AND ZINC BY PRECIPITATION WITH AMMONIA

In these experiments 250 mg. of one of the elements in the first column was precipitated from a solution containing 250 mg. of one of the elements listed at the top of the four major columns.

Element precipitated	Expt.	Proce-dure	Mn in ppt. mg.	Notes	Expt.	Proce-dure	Ni in ppt., mg.	Notes
		Manganese				Nickel		
Chromium	1	I	55	1	6	I	114	
	2	II	0.8		7	I	163	4
	3	II	0.4	2	8	I	150	5
	4	II	0.5	3	9	II	28	
	5	III	18	2	10	II	26–28	6
					11	III	35	
Aluminum	19	I	4.0		23	I	230	
	20	II	0.2		24	II	10	
	21	II	0.3		25	III	190	
	22	III	2.5					
Ferric iron	35	I	2.0		39	I	16	
	36	II	1.5		40	II	3–4	6
	37	II	0.8		41	III	8–10	6
	38	III	2.7		48	III	13	10,11
					49		13	10,11

TABLE I   (*Concluded*)

Element precipitated	Expt.	Proce-dure	Co in ppt., mb.	Notes	Expt.	Proce-dure	Zn in ppt., mg.	Notes
		—Cobalt—				—Zinc—		
Chromium	12	I	160		16	I	212	
	13	II	34		17	II	41	
	14	II	61	7	18	III	165	
	15	III	90					
Aluminum	26	I	230		31	I	214	
	27	I	216		32	II	75	
	28	II	8		33	III	121	
	29	III	166		34	II	68	9
	30	I, II	23	8				
Ferric iron	42	I	16		45	I	106	
	43	II	4		46	II	11	
	44	III	8		47	III	27	
					50	III	21	10
					51		19	10

NOTES TO TABLE I

1. The manganese in this precipitate was separated by precipitation as dioxide by addition of potassium chlorate to a nitric acid solution. The precipitate was washed free of chromate and chlorate and the manganese determined iodometrically.

2. The chromium hydroxide precipitate obtained in Expt. 3 required about 100 ml. of wash solution. However, the precipitate in Expt. 5 required 500 ml. The washings were tested for manganese by addition of ammonia and hydrogen peroxide.

3. In this neutralization a slight excess of ammonia was added, so 6 normal hydrochloric acid was added until the methyl red was distinctly pink and the neutralization repeated.

4. A slightly larger excess of ammonia was added in Expts. 7 and 8 than in 6.

5. Five grams of ammonium chloride was used in addition to that formed by neutralization of the hydrochloric acid.

6. The nickel was estimated by comparing with standards the precipitate produced by dimethylglyoxime in one-tenth the filtrate.

7. The solution was made just neutral to litmus without using a reference solution with an internal indicator. Probably slightly more ammonia was added than in Expt. 13.

8. The volume and other conditions were as in Procedure I. Neutralization was made and an excess of ammonia avoided as in Procedure II.

9. Only 160 mg. of zinc was taken.

10. In Expts. 49 and 51 an excess of 5 ml. of 15 normal ammonia was added; otherwise Expts. 48 and 49 and Expts. 50 and 51 were carried out in exact duplicate to note the effect of the larger excess of ammonia.

11. Expts. 48 and 49 were carried out in this Laboratory by Mr. Francis Hunter and Mr. Elvin Lien.

Discussion of the Data of Table I

An inspection of the data in Table I would seem to lead to two general conclusions: first, in about half of the separations studied the separation is quite unsatisfactory even under the most favorable conditions. Second, in every case studied the separation is more effective when an

excess of ammonia is avoided and, in most cases, unless this excess is avoided the separation is so imperfect that little is gained by reprecipitations; thus, under the conditions studied, when an excess of ammonia is added, more than 50% of the nickel, cobalt or zinc is carried out by either chromium or aluminum. This would seem to indicate that the ammonia separation is more effectively carried out, at least in dilute solutions, as a process of selective hydrolysis and not as one depending on the formation of the soluble complex ammino ions. In support of this it is to be noted that manganese, where the tendency toward this complex formation is least, is much less co-precipitated than nickel, cobalt or zinc.

Also, the P_H values at which these divalent elements are precipitated from solution are given by Britton[10] as follows: zinc, 5.2; nickel, 6.7; cobalt, 6.8; and manganese, 8.5–8.8. It is seen that the co-precipitation in the experiments carried out by Procedure II in every case varies in amount in this same order—zinc, the least soluble hydroxide, showing the greatest tendency to be carried with the precipitate. The same order in general holds for the experiments by Procedures I and III, which is somewhat surprising, as, with an excess of ammonia present, it would be expected that the formation of the soluble ammonia complexes would be a more deciding factor; for the same reason it would have been predicted that the large excess of ammonia added in Expts. 49 and 51 would have decreased markedly the amount of co-precipitation; however, the difference is within the experimental variations. That the effect is due to an adsorption process and not to mechanical inclusion or local precipitation is indicated by the experiments of Ibbotson and Brearly[11] and of Noyes and Bray,[12] showing that when an ammoniacal solution of the bivalent element is added to a suspension of the freshly precipitated hydroxide, the effect approaches that obtained by precipitation in the presence of the bivalent element. That the complex ammonia compounds are not extensively carried down was shown by the fact that relatively little ammonia was found upon analyzing an aluminum precipitate, produced by Procedure III, which had co-precipitated with it about 200 mg. of nickel. Further studies are being made of certain of these separations in which the co-precipitation is pronounced in an attempt to ascertain the various factors affecting it and the mechanism of the phenomenon.

Specifically, in addition to confirming the results of Lundell and Knowles that, by proper methods of neutralization, a satisfactory separation of manganese from aluminum and from iron is obtained, it is shown that under these same conditions manganese can be separated from chromium. However, it is to be noted that the co-precipitation of manganese is in-

[10] Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1929, p. 254, 278.
[11] Ibbotson and Brearly, Chem. News, 81, 193 (1900).
[12] Ref. 3, p. 154.

creased much more by an excess of ammonia in the separation from chromium than it is in the separation from either aluminum or iron. The separations of nickel from aluminum and chromium show from 50 to 90% of this element brought down when an excess of ammonia is added, demonstrating the futility of reprecipitations; the same general behavior is obtained with these elements and cobalt. Even under the most favorable conditions these separations are hardly adequate for quantitative work. The separations of nickel and cobalt from iron, made from carefully neutralized solutions, show about 2% co-precipitation so that a reprecipitation would probably reduce this to satisfactory limits. The separation of zinc under these conditions is unsatisfactory regardless of methods of neutralization. It is to be noted that the co-precipitation in method I is usually greater than that in method III, showing the favorable effect of an increased volume with thereby a decrease in the concentration of the co-precipitated substance.

It is perhaps worthy of note that the procedure, almost universal in qualitative textbooks, which directs that a *slight excess* of ammonia be added to a relatively small volume of solution, produces conditions which are apparently the *least* favorable of those studied for the separations desired.

The Ardagh Method of Carrying out the Ammonia Separation.— Recognizing the inadequate nature of the conventional ammonia precipitation for the separation of iron (and aluminum) from zinc, Ardagh and his co-workers[13,14] have devised a procedure for carrying out the separation which employs radically different conditions from those existing in any of the procedures thus far described. In it the precipitation is made by the addition of a large excess of 15 N ammonium hydroxide to a very small volume of an acid solution which has been previously saturated with solid ammonium chloride. These conditions produce a more compact and granular precipitate than that usually formed and a satisfactory separation of zinc from iron or aluminum is obtained by a single precipitation. An extension of this method to other separations would seem desirable and, since no such data seemed available, such a study was made and the results are shown in Table II. The general procedure used was as follows. A hydrochloric acid solution of the elements to be separated was evaporated to a volume of 3 to 5 ml., cooled and 5 g. of solid ammonium chloride then intimately mixed with the solution. Following this 10 ml. of 15 N ammonium hydroxide was added, the resulting mixture thoroughly mixed with a stirring rod, 25 ml. of water added and the precipitate filtered, usually equally dividing it between two separate filters in order to facilitate washing. The precipitates were washed with a solution containing 5 g. of ammonium chloride and 5 ml. of 15 N ammonium hydroxide in a volume of 100 ml.

[13] Ardagh and Broughall, *Can. Chem. Met.*, **7**, 198 (1923).
[14] Ardagh and Bongard, *Ind. Eng. Chem.*, **16**, 297 (1924).

Variations from this procedure are explained in the notes accompanying the table. It should be mentioned that chromium cannot be precipitated under the conditions of this procedure as it remains to a large extent in solution due to the formation of complex ammines. Also from 2–5 milligrams of aluminum is dissolved and has to be recovered subsequently from the filtrate.

In these experiments 250 milligrams of one of the elements listed in the first column of the table was taken together with 250 milligrams of one of the elements listed at the top of the four major columns. Observations and variations from the outlined procedure are contained in the notes to the table.

TABLE II

THE SEPARATION OF ALUMINUM AND IRON FROM MANGANESE, NICKEL, COBALT AND ZINC BY THE ARDAGH METHOD OF PRECIPITATION WITH AMMONIA

In each experiment 250 mg. of one of the elements in the first column was taken with 250 mg. of one of the elements listed at the top of the four main columns

Element precipitated	Manganese Found in ppt.			Nickel Found in ppt.,			Cobalt Found in ppt.,			Zinc Found in ppt.,		
	Expt.	mg.	Notes	Expt.	mg.	Notes	Expt.	mg.	Notes	Expt.	mg.	Notes
Aluminum	1	64	1	3	4	3	4	4	4	5	15	5, 8
	2	105	2							6	8	6, 8
										7	2	7, 8
											0–0.4	14
Iron	8	25		10	0.1–0.2		11	25	10	14	0.5	12
	9	8	9	16	0.7–0.9	13	12	5	10	15	0.6	13
							13	6	11		0.2–0.5	14

NOTES TO TABLE II

1. The precipitate was equally divided between two filters and each half required 150–200 ml. of wash solution; it darkened during the washing.

2. Only 5 cc. of 15 N ammonium hydroxide was used.

3. Found 5 mg. of aluminum in the filtrate.

4. Filtration and washing difficult; 200 ml. wash solution required.

5. Only 2 ml. of 15 N ammonium hydroxide was added and the mixture was diluted to 50 ml. before filtering. Less than 0.5 mg. of aluminum remained in the filtrate.

6. Only 3 ml. of ammonia added, mixture diluted to 25 ml. 1–2 mg. of aluminum found in filtrate.

7. Only 5 ml. ammonia added. 2–3 mg. of aluminum in filtrate.

8. In Expts. 5, 6, 7 only 125 mg. of aluminum was taken with 250 mg. of zinc.

9. Only 5 ml. of ammonia added.

10. In this experiment (No. 11) the original solution was evaporated to 3–4 ml. and this solidified upon cooling. Two ml. of 6 N hydrochloric acid was added to dissolve this residue. Upon adding the ammonium chloride this solution was absorbed and even after long maceration with a stirring rod the mixture did not seem homogeneous. In Expt. 12 the original solution was evaporated to 5 ml. and after adding the ammonium chloride, 6 N hydrochloric acid was added (2 cc.) until a homogeneous, thoroughly wet mixture was obtained.

11. A repetition of Expt. 12, except that the mixture was heated to 70–80° before filtering and the wash solution was also heated. The precipitate was more difficult to wash, requiring 500 ml. of wash solution.

12.   5 g. of ammonium nitrate was used instead of ammonium chloride.

13.   A nitric acid solution was evaporated to 3–4 ml. and 8 g. of ammonium nitrate used instead of the ammonium chloride. Ammonium nitrate was substituted for ammonium chloride in the wash solution.

14.   Values taken from experiments of Ardagh and Bongard[14] using about 200 mg. of iron and zinc.

Discussion of the Data of Table II

An inspection of the data of Table II, and a comparison with Table I, shows, as was to be expected, that the Ardagh method cannot be used for separations involving manganese, due to the oxidation of this element in the more alkaline solution. The separation of nickel from aluminum is improved and the separation of nickel from iron is so nearly perfect that only one precipitation would be required for most quantitative work. The separation of cobalt from aluminum is more complete than by any method of precipitation by ammonia in a dilute solution; although the separation of cobalt from iron is fairly satisfactory it is no more complete than that obtained by a careful neutralization. Where, as is the case in many qualitative systems, it is desired to separate iron from nickel, cobalt and zinc, the Ardagh method of precipitation offers decided advantages.

Attempts to reduce the amount of aluminum dissolved by decreasing the ammonia concentration caused, in the separation from zinc, an increase in the co-precipitation of that element (Expts. 5, 6, 7). This indicates that in this separation, contrary to those studied in Table I, the bivalent elements are held in solution mainly due to the formation of the ammonia complexes. That, in spite of the use of small volumes and more concentrated solutions, better separations are obtained by this method, is probably due to this more complete conversion of the bivalent elements into the ammonia complexes and, in addition, to the more granular and less hydrous nature of the precipitates obtained, these physical characteristics usually indicating a less effective adsorbing agent.[15] Experiments 14, 15 and 16 show that the substitution, in the cases studied, of an equivalent amount of ammonium nitrate for ammonium chloride has relatively little effect, indicating that the presence of chloride ion is not highly essential to the separation.

The Separation of Bismuth from Copper and Cadmium

In most systems of qualitative analysis this separation follows the detection and removal of lead as sulfate. In precipitating lead the solution is fumed with sulfuric acid, then cooled and diluted. To conform to these conditions the procedure used was as follows: to 250 mg. each of bismuth and of copper or cadmium (as the nitrates), was added 10 ml. of 6 N sulfuric acid and the volume made from 80–100 ml. There was then added

---

[15] Weiser, "The Hydrous Oxides," The McGraw-Hill Book Co., New York, 1926, p. 1.

6 *N* ammonia until in one case the solution was just neutral to litmus or, in the alternative case, there was 5 ml. of ammonia in excess. The precipitates were washed with 2% ammonium sulfate solution and then analyzed for the copper and cadmium present. In the separations in which the solution was made just neutral and an excess of ammonia was avoided, 150–180 mg. of copper and 2 mg. of cadmium were found in the bismuth precipitates; in the separations with the 5 ml. excess of ammonia added 0.5 mg. of copper and 2 mg. of cadmium were found. This indicates, as would be expected from the P_H value at which copper precipitates, that the separation of copper from bismuth in a sulfate solution requires an excess of ammonia sufficient to form the complex ammine; on the other hand, the separation of cadmium, due to the greater solubility of the hydroxide, is equally effective with or without an excess of ammonia.

Summary

Data are presented for the separation of chromium, aluminum and iron from manganese, nickel, cobalt and zinc by various modifications of the ammonia separation.

It is shown that when working with the usual dilute solutions the separation is more effective when a careful neutralization is made using methyl red (or its equivalent) as indicator, and an excess of ammonia avoided. Under these conditions, with 250 mg. of each element present, the chromium precipitate carried out only 0.4–0.8 mg. of manganese, but 30–40 mg. of nickel, cobalt or zinc; the aluminum precipitate carried out only 0.2–0.3 mg. of manganese, but 8–10 mg. of nickel or cobalt and 75 mg. of zinc; the iron precipitate carried out 0.8–1.5 mg. of manganese, 3–4 mg. of cobalt or nickel and 11 mg. of zinc.

When an excess of ammonia is used the separation is so imperfect, regardless of the presence of a large amount of ammonium chloride, that in the majority of cases it is not recommended even for qualitative purposes.

When the precipitation is made by addition of concentrated ammonium hydroxide to a small volume (3–5 ml.) of a solution saturated with ammonium chloride, even with 250 mg. of each element present, less than a milligram of the soluble element was co-precipitated in separating iron from nickel or zinc, or aluminum from zinc, and 4–5 mg. was co-precipitated in separating iron from cobalt, or aluminum from nickel or cobalt. Under the conditions of the procedure aluminum dissolves to the extent of about 5 mg., and chromium is very soluble.

When separating bismuth from copper in a dilute sulfate solution an excess of ammonia is required; the separation from cadmium can be made either from a carefully neutralized solution or one containing an excess of ammonia.

PASADENA, CALIFORNIA