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## STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. II. THE SEPARATION BY MEANS OF SODIUM HYDROXIDE AND SODIUM PEROXIDE

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**Introduction.**—As stated in the first paper of this series, the data here presented were collected 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.

The use of sodium hydroxide and sodium peroxide as a group reagent in a qualitative system seems to have been first suggested by Parr,<sup>1</sup> who used it to effect the separation of iron, manganese, nickel and cobalt from aluminum, chromium and zinc and it was later adopted by Noyes, Bray and Spear<sup>2</sup> in their system which included many of the less common elements. The process has also been used extensively in qualitative systems, and in quantitative methods for the separation of the individual elements of one of these groups from those of the other. Frequently in quantitative methods other oxidizing agents, such as bromine, chlorine or persulfate, are substituted for the peroxide but these are not as convenient as the peroxide or may introduce objectionable ions into the analysis.

Statements in the literature as to the effectiveness of these individual separations are somewhat incomplete and often not definite. Noyes, Bray and Spear state that: "The separation of the two groups by this process is entirely satisfactory, at any rate, from the standpoint of qualitative analysis, with the single exception that when 5 or 10 mg. of zinc are present this may be carried down completely when elements of the iron group (especially manganese) are present in large quantity." However, there appears to be a certain amount of distrust of the method which is perhaps explained by the statement of Hillebrand and Lundell:<sup>3</sup> "The use of sodium hydroxide for precipitations has not been in good repute among analysts because of the uncertain quality of the reagent and the slimy character of the solution and precipitate." It is explained, however, that the first objection is not as well founded today as in the past, that the difficulty in filtering about 5% solutions is not serious, and that: "In the hands of one of us (L.) the method has proved very satisfactory."

The confirmatory experiments and test analyses of Noyes, Bray and

<sup>1</sup> Parr, *THIS JOURNAL*, **19**, 341 (1897).

<sup>2</sup> Noyes, Bray and Spear, *ibid.*, **30**, 484 (1908).

<sup>3</sup> Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 76.

Spear give quite complete information as to the qualitative value of the separation, as they perform it, in the detection of small amounts of an element in the presence of even large amounts of others; however, very meager systematic data seem to be available showing the completeness of the individual separations when considerable amounts of each element are present. Such data have been collected and are presented in this paper.

This study has been restricted to the common elements which may be found in the ammonium sulfide precipitate and therefore includes only the separation of iron, manganese, nickel and cobalt from aluminum, chromium and zinc. For more general statements concerning certain of the individual separations, as well as for references to the original literature, one is referred to Hillebrand and Lundell<sup>3</sup> and to Rüdüsüle.<sup>4</sup>

### Experimental Procedure

The separations have been carried out according to two general procedures. The first of these, called Procedure I, conforms closely to that given by A. A. Noyes<sup>5</sup> and by Noyes and Bray,<sup>6</sup> and more nearly represents the usual qualitative technique. It was as follows.

To a solution of the elements to be separated, containing 1-2 ml. of 6 *N* hydrochloric acid and having a volume of 30-40 ml., was added 6 *N* sodium hydroxide until the solution was alkaline to litmus, and then 5 g. of sodium peroxide. The sodium peroxide was sprinkled in very gradually and the mixture kept cold during the addition. Then the mixture was boiled until the sodium peroxide was decomposed, diluted to 60 ml. and filtered through hardened filters; in order to facilitate washing, two separate filters were used if the precipitate was bulky. The precipitate was washed with hot water until the washings no longer turned red litmus blue.

In Procedure II certain modifications were used which are recommended as giving more quantitative separations. It was as follows.

To a solution of the elements to be separated, containing 1-2 ml. of 6 *N* hydrochloric acid and having a volume of 15-20 ml., 6 *N* sodium hydroxide was added dropwise until the first permanent turbidity was produced. To this was added 20 ml. of 3% hydrogen peroxide and the resulting solution poured dropwise into 100 ml. of 5% sodium hydroxide which was kept just boiling during this addition. The mixture was then cooled and kept cool during the slow addition of 5 g. of sodium peroxide. Finally the mixture was boiled until the sodium peroxide was decomposed and then filtered, two separate papers being used in most cases. Hardened filters were not necessary in filtering these solutions. The precipitate was washed with 50 ml. of hot 5% sodium hydroxide and then with a hot 1% solution until no test for the soluble element being separated was obtained.

The slightly acid solution containing the hydrogen peroxide was poured into the hot sodium hydroxide solution since there appears to be general agreement that a better

<sup>4</sup> Rüdüsüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Max Drechsel, Bern.

<sup>5</sup> Noyes, "Qualitative Chemical Analysis," The Macmillan Company, New York, 1922, 9th ed., p. 95.

<sup>6</sup> Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927, pp. 164, 168.

separation results from this order of mixing.<sup>7</sup> Qualitative experiments also indicated that a more rapid and complete oxidation of chromium was obtained when hydrogen peroxide was present in the acid solution; when sodium peroxide was added to an alkaline solution, as in Procedure I, or upon adding an acid solution without peroxide to a hot sodium hydroxide solution, a precipitate which oxidized slowly was obtained. The acid solution could be added to a cold sodium peroxide solution; however, the preparation of a solution of sodium peroxide, even when it is kept cold, results in excessive loss of peroxide due to its decomposition. Furthermore, the precipitate produced upon addition of the acid solution to the hot hydroxide seemed more readily handled than that formed by precipitating in the cold and then heating.

In most of the experiments 250 mg. of the element to be precipitated was taken with 250 mg. of one of the soluble elements. The precipitate was then analyzed in order to determine the amount of the soluble element carried down. The results of these experiments, showing the amount of the soluble element carried down in each case, have been collected in Table I which is shown below. Observations and variations from the procedure outlined above are contained in the notes to the table. For the reason stated in the first paper of this series,<sup>8</sup> it is felt that significance should be given to the general magnitude, rather than the exact value, obtained in any individual experiment.

**Methods of Analyzing the Precipitates.**—The general methods used in analyzing the precipitates are here described. Changes or modifications in individual experiments are given in the notes which follow Table I.

The precipitates were in all cases dissolved in hot hydrochloric acid, sodium sulfite or hydrogen peroxide being used to help dissolve the manganese and cobalt precipitates.

The aluminum was recovered from the solution of the manganese precipitates by carefully neutralizing the boiling solution with ammonium hydroxide, avoiding an excess. The amount of aluminum in the precipitate thus obtained was estimated by comparing it with standard precipitates prepared under strictly similar conditions. The chromium in the manganese precipitate was recovered from the reduced hydrochloric acid solution by careful neutralization with ammonium hydroxide. The chromium hydroxide precipitate was dissolved and treated with sodium peroxide; any manganese dioxide present was filtered out and the chromate in the filtrate determined iodometrically. Zinc was recovered from the hydrochloric acid solution by fuming it with sulfuric acid, carefully neutralizing it, adding the proper excess of sulfuric acid and precipitating the zinc as sulfide. The precipitate was washed and introduced into an excess of ferric sulfate solution. The ferrous iron thus produced was titrated with standard permanganate solution.

After dissolving the ferric hydroxide precipitates in 6 *N* hydrochloric acid, the iron was removed by extraction with ether. The elements remaining in the aqueous solution were then estimated as indicated above.

The aluminum was recovered from the solution of the cobalt precipitates by carefully neutralizing the boiling solution with ammonium hydroxide;

<sup>7</sup> Ref. 4, Vol. V, pp. 96, 900, 1105; Ref. 3, p. 77.

<sup>8</sup> THIS JOURNAL, 54, 2219 (1932).

the precipitate thus obtained was dissolved, reprecipitated and compared with standards. The chromium, after reduction, was precipitated with ammonium hydroxide; this precipitate was dissolved and treated with sodium peroxide to remove the co-precipitated cobalt and to oxidize the chromium; after filtering out the cobalt oxide, the chromium was determined iodometrically. The zinc was recovered by precipitation as sulfide from a sulfuric acid solution. This precipitate was dissolved and treated with sodium peroxide to remove the co-precipitated cobalt. The zinc was again precipitated as the sulfide and determined as indicated above.

The aluminum in the hydrochloric acid solution of the nickel precipitates was recovered by carefully neutralizing with ammonium hydroxide; the aluminum hydroxide precipitate thus obtained was treated with sodium hydroxide and potassium persulfate to remove the nickel carried down, a final precipitation of the aluminum with ammonium hydroxide made, and this precipitate compared with standards. The chromium and zinc were recovered by the methods used in analyzing the solution containing cobalt.

TABLE I

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

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 one of the three major columns.

Element precipitated 250 mg. taken	Aluminum, 250 mg. taken				Chromium, 250 mg. taken				Zinc, 250 mg. taken			
	Expt.	Meth- od	Al found in ppt., mg.	Notes	Expt.	Meth- od	Cr found in ppt., mg.	Notes	Expt.	Meth- od	Zn found in ppt., mg.	Notes
Manganese	1	I	12-15	1, 2	3	I	50-70	3	29	I	65	6
	2	II	2-3		4	II	51	4, 5	5	II	60	6
					25	I	7	10				
Iron (ferric)	6	I	1-2	1, 2					9	I	103	7
	7	II	1-2		8	II	56		10	II	37	6
					24	I	37		32	II	47	
					24	I	0.2	10	33	II	46	
									34		67	11
Cobalt	28	I	20-25		12	I	65-80	8	35		62	11
	11	II	12-15		13	I	65		30	I	50	6
					14	I	87	9	16	II	88	6
					15	II	21					
					23	II	1	10				
Nickel	17	I	30-35		27	I	44		31	I	30	6
	18	II	30-40		19	II	42		21	II	25	
					22	II	0.6-1	10				

## NOTES TO TABLE I

1. Only 125 mg. of aluminum was taken.
2. The aluminum was recovered from the precipitate by dissolving it in hydrochloric acid, repeating the sodium hydroxide-sodium peroxide treatment, acidifying this filtrate, making it just alkaline with ammonium hydroxide and comparing the aluminum hydroxide precipitate obtained with standards.
3. The chromium was recovered from the precipitate by dissolving it in hydro-

chloric acid, repeating the sodium hydroxide-sodium peroxide treatment, making this filtrate just acid with acetic acid and precipitating the chromate as lead chromate. The precipitate was matched with standards. Method uncertain due to retention of chromium in second precipitate and to uncertainty in matching the size of the precipitate of lead chromate.

4. The color of the solution indicated that the chromium was completely oxidized upon pouring the acid solution containing hydrogen peroxide into the sodium hydroxide.

5. Difficulty was had in washing the precipitate free of chromate.

6. Only 160 mg. of zinc was taken.

7. The zinc was estimated by precipitation as carbonate, dissolving this in an excess of standard acid and titrating back with standard base.

8. The chromium was estimated by repeating the sodium hydroxide-sodium peroxide treatment, precipitating the chromium in the second filtrate as lead chromate and matching the precipitate. See note 3.

9. The hydrochloric acid solution of the precipitate was evaporated, a large excess of 16 *N* nitric acid added, 4 g. of potassium chlorate slowly sprinkled in, and the solution boiled until the excess chlorate appeared to be decomposed. The solution was made alkaline with ammonium hydroxide, then just acid with acetic acid, and the chromate precipitated as lead chromate. This was filtered out, dissolved in hydrochloric acid and the chromate determined iodometrically.

10. The chromium was taken as potassium chromate and no hydrogen peroxide was added to the acid solution, otherwise a duplication of Expt. 19.

11. Duplicates of Expts. 32 and 33, except that the sodium hydroxide was added to the acid solution instead of the reverse order.

**Discussion of the Data of Table I.**—From the cases studied it would seem that, in general, the separations obtained by the two procedures are not strikingly different. To test the effectiveness of the method of adding the acid solution to the sodium hydroxide, Expts. 32-35 were carried out by Mr. Elvin Lien and Mr. James Radford. In all of these the conditions of Procedure II were duplicated, except that in Expts. 34 and 35 the 5% sodium hydroxide was added to the acid solution containing the hydrogen peroxide; this resulted in a definite increase in the zinc carried out. Where better separations are obtained by Procedure I, it seems probable that the higher concentration of sodium hydroxide at first obtained in that procedure is the deciding factor. It has been found in practice, however, that the results obtained in repeating the same separation by Procedure I vary more than do those by Procedure II.

More specifically, the separation of aluminum from manganese and iron can be made sufficiently complete for qualitative and for most quantitative work; with the amounts of each element here used, from 4 to 5% of the aluminum is left with the cobalt precipitate and from 12-14% with the nickel precipitate; this latter difficulty is generally recognized.<sup>9,10</sup>

The separation of chromium, beginning with chromic ion and using sodium peroxide as the oxidizing agent, is unsatisfactory in every case

<sup>9</sup> Ref. 4, Vol. V, p. 242.

<sup>10</sup> Ref. 3, pp. 77, 391.

regardless of method. That this is due to incomplete oxidation of the chromium by the peroxide is shown by Expts. 20-23, where, beginning with the chromium as chromate, satisfactory separations are obtained except in the case of manganese and there the co-precipitation is reduced from 20% to about 3%. We are indebted to Mr. Harrison Backus for the following experiments showing that only trivalent chromium is co-precipitated.

To 250 mg. of chromium and 250 mg. of nickel, as the chlorides, in 50 ml. of a solution containing 4 ml. of 6 *N* hydrochloric acid, was added 6 *N* sodium hydroxide until the first turbidity appeared, then 10 ml. of 3% hydrogen peroxide; this was slowly poured into a cold solution of 20 ml. of 6 *N* sodium hydroxide and 10 ml. of 3 *N* sodium carbonate to which had been added 1 g. of sodium peroxide. An additional gram of sodium peroxide was added during the mixing of the solution, then 3 g. more was slowly sprinkled in; finally, the mixture was boiled for three minutes after no more oxygen bubbles seemed to be evolved.

The precipitate was filtered out, washed thoroughly with hot water, dissolved in sulfuric acid and this solution made alkaline with ammonia; a precipitate of chromium hydroxide was obtained which was estimated to contain about 50 mg. of chromium. No test for chromate could be obtained in the solution. Further experiments showed that under the conditions of the above experiment chromium, when *alone*, was completely oxidized—the oxidation was slow in a cold solution, but proceeded rapidly when the mixture was heated. Also, it was found that when chromate was added to a nickel precipitate produced by sodium peroxide under the conditions of this experiment and this mixture then acidified with sulfuric acid, less than one milligram of the chromium was reduced, thus showing that the reduced chromium originally obtained could not have been due to peroxide held by the nickel precipitate. The adsorption of colloidal hydrous chromic oxide by precipitates of iron, manganese, cobalt and nickel frequently has been noted,<sup>11</sup> and it would be expected that the chromium thus held would be oxidized with difficulty. It is therefore recommended that chromium be oxidized to chromate in an acid solution before using the sodium hydroxide-sodium peroxide separation.

There is considerable evidence that alkaline solutions of chromate may be reduced by filter paper,<sup>12,13,14</sup> the effect apparently being dependent upon the quality of the paper, the temperature of the solution and the time of contact. To note the extent of this effect experiments were carried out by Mr. Backus in which solutions containing 250 mg. of chromium as chromate in 15 ml. of 4 *N* sodium hydroxide were heated to boiling and then filtered through four different types of paper filters—two qualitative papers of different price, a quantitative paper and a hardened paper. The solutions were kept hot and the rate of flow restricted so that the filtrations required from 6 to 10 minutes. There was no apparent color change of the solutions on the filters or in the filtrates. The filtrates were then acidified with sulfuric acid. There was produced in the filtrate from the cheaper qualitative paper a considerable precipitate of what appeared to be paper pulp; the filtrate from the other qualitative paper became slightly cloudy, while the other filtrates remained quite clear. The acid solutions were filtered and then made just alkaline with ammonium hydroxide. None of the solutions produced an observable precipitate. This indicates that the reduction of an alkaline chromate

<sup>11</sup> Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, p. 90.

<sup>12</sup> Jervis, *Chem. News*, **77**, 133 (1898).

<sup>13</sup> Allison, *ibid.*, **96**, 1 (1907).

<sup>14</sup> Mellor, "A Treatise on Quantitative Inorganic Analysis," Griffin, London, p. 477.

solution by filtration through paper filters is so small as to be inappreciable in its effect on qualitative or most quantitative separations.

The separation of zinc from the elements precipitated by sodium hydroxide is unsatisfactory in every case studied, from 10–50% of the zinc remaining in the precipitate.

### Summary

An experimental study of the separation of manganese, iron, cobalt and nickel from aluminum, chromium and zinc by means of sodium hydroxide and sodium peroxide has been made.

With 250 mg. of each element present, from 1–3 mg. of aluminum remains with the manganese or the iron, from 12–15 mg. with the cobalt, and 30–40 mg. with the nickel.

The separation of trivalent chromium from these elements is unsatisfactory due to incomplete oxidation of the chromium. When the chromium is originally present as chromate, not over 1 mg. is carried down by any of the precipitates except manganese, where 7 mg. was co-precipitated.

The separation of zinc is unsatisfactory, from 10–40% of it being carried down with the precipitates.

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## STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. III. A NEW METHOD FOR THE SEPARATION OF ZINC, COBALT, NICKEL AND IRON FROM ALUMINUM, CHROMIUM AND MANGANESE

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### Introduction

The two methods most frequently used in systems of qualitative analysis for dividing into sub-groups the elements found in the ammonium sulfide precipitate are: (1) the ammonium hydroxide precipitation, and (2) the sodium hydroxide–sodium peroxide treatment. The results of studies of these separations have been presented in the two preceding papers of this series,<sup>1</sup> and the data show that many of the individual separations obtained by either of these methods are so incomplete as to make their use unsatisfactory in a qualitative system in which it was desired to stress the quantitative information that could be obtained. Accordingly, other methods for separating these elements into groups were investigated.

<sup>1</sup> (a) Swift and Barton, *THIS JOURNAL*, **54**, 2219 (1932); (b) Swift and Barton, *ibid.*, **54**, 4155 (1932).