

A REVISED PROCEDURE *for the* QUALITATIVE ANALYSIS *of* GROUP III CATIONS*

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INTRODUCTION

A METHOD for the quantitative separation of iron, aluminum, and chromium from the divalent ions of Group III has been proposed by Kolthoff, Stenger, and Moskovitz.¹ The method, which makes

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¹ KOLTHOFF, I. M., V. STENGER, AND B. MOSKOVITZ, *J. Am. Chem. Soc.*, **56**, 812 (1934).

use of a benzoic acid-ammonium benzoate buffer for the precipitation of the trivalent ions as complex benzoates at a pH of 3.8, has been successfully adapted to a simple scheme of qualitative analysis for student use.

The benzoate procedure affords a number of advantages. A complete separation of the hydrous oxides from the divalent ions of the group is readily effected. Since the separation is carried out at a low pH there is no danger of the partial precipitation of

the hydroxide or oxy-hydroxide of manganese. In addition, the basic benzoates obtained as precipitates are very readily coagulated and may be rapidly filtered from the warm solution. The slimy and difficultly filterable precipitate obtained in the simple ammonia separation is thus avoided. The division of the Group III ions into two sub-groups minimizes the number of separations necessary and reduces the attendant errors.

A modified procedure for the separation and identification of the divalent ions of the group has been devised. The troublesome separation of the sulfides of nickel and cobalt from those of manganese and zinc by the use of cold 1 *N* hydrochloric acid is avoided. The detection of zinc is thus made easy. The separation and detection of manganese is complete and simple.

Student results with the new procedure have been compared with those obtained by the use of the conventional scheme of analysis. These results seem to justify the use of the new procedure. The procedures described below have been adapted for student unknowns of 20 ml. containing 40 mg. of each ion calculated as the metal.

PROCEDURE

1. *Preparation for Precipitation.*—Unless the solution to be analyzed is the filtrate from Group II, in which case dichromate, permanganate, and chromate ions have already been reduced, it is necessary to reduce these ions here. Make the solution acid to litmus with 5 *N* hydrochloric acid, and add 3 ml. in excess. Carefully add two or three drops of formalin and boil the solution until the excess formaldehyde is removed. If the solution to be analyzed is the filtrate from Group II, or if ferrous ions are present, they must be oxidized to the ferric state. Add 1 ml. of concentrated nitric acid and boil the solution for a few minutes to effect this oxidation.

2. *Precipitation of Group III(A).*—Add 3 *N* ammonium hydroxide to the solution from (1), drop by drop, until a very faint precipitate persists on stirring. If no precipitate forms it indicates the absence of Group III(A) ions. Add 1 ml. of glacial acetic acid and 1 g. of solid ammonium chloride, dilute to 100 ml., and then add 25 ml. of a ten per cent. solution of ammonium benzoate. Boil gently for three minutes; stir to avoid frothing. Filter the solution while hot. Aluminum gives a white, iron a tan, and chromium a gray-green precipitate. The filtrate, which may deposit crystals of benzoic acid, is retained for the analysis of Group III(B).

3. *Analysis of Group III(A).*—Remove the precipitate of benzoates from the filter paper and treat with 20 ml. of 2 *N* hydrochloric acid. Warm the solution until all metallic benzoates have been dissolved and only white benzoic acid remains. Cool the solution, filter off the benzoic acid, and wash the precipitate thoroughly. Discard the precipitate.

The procedure for the separation and identification

of iron, aluminum, and chromium now follows the conventional scheme.²

4. *Precipitation of Group III(B).*—Make the filtrate from (2) basic with ammonium hydroxide, heat nearly to boiling, and pass in hydrogen sulfide gas for three minutes. Filter and wash the precipitate. Immediately after filtering, acidify the filtrate with acetic acid and boil down to approximately 20 ml. Cool the solution and filter off the benzoic acid. Removal of the benzoic acid at this point will aid in the coagulation of colloidal sulfides. Treat the filtrate according to the procedures for Groups IV and V.

5. *Separation of Manganese.*—Dissolve the sulfides from (4) by warming with 20 ml. of 6 *N* nitric acid. Pick off the sulfur with a cold spatula. Add 10 ml. of concentrated nitric acid and then 1 g. of solid potassium chlorate. Boil the solution down to 10 ml. or less. Manganese separates as hydrated manganese dioxide which is brown to black.

6. *Tests for Manganese.*—(a) The brown to black precipitate in (5) may be considered a test for manganese.

(b) Filter the precipitate of manganese dioxide from (5) and wash. Dissolve the precipitate in 5 ml. of 5 *N* nitric acid containing a few drops of hydrogen peroxide. Boil to destroy the excess peroxide, add an equal volume of concentrated nitric acid, and then add 0.5 g. of solid lead tetroxide. Boil the solution and allow the excess lead tetroxide to settle to the bottom. The purple color of the permanganate ion in the supernatant solution is a confirmatory test for manganese.

7. *Separation of Zinc.*—Make the filtrate from (5) just alkaline with 5 *N* sodium hydroxide and then add 5 ml. in excess. Heat the solution just to boiling, filter while warm, and wash the precipitate.

8. *Tests for Zinc.*—(a) Neutralize the filtrate from (7) with acetic acid and add 2 drops in excess. Divide the solution into two parts. Pass hydrogen sulfide gas into the first portion. The formation of a white precipitate is a test for zinc.

(b) To the second portion add about ten drops of a five per cent. solution of 8-hydroxy-quinoline in 2 *N* acetic acid. The formation of a yellow precipitate is a delicate test for zinc.

9. *Solution of the Hydroxides of Nickel and Cobalt.*—Dissolve the precipitate from (7) by pouring 15 ml. of warm 2 *N* hydrochloric acid through the paper several times.

10. *Test for Nickel.*—To 5 ml. of the solution from (9) add ammonium hydroxide until the solution is just alkaline to litmus and then 1 ml. in excess. To this solution add a one per cent. solution of dimethylglyoxime in alcohol, a few drops at a time until a scarlet precipitate has been obtained, or until a total of 5 ml. has been added. A scarlet precipitate is a test for nickel. A light brown coloration in the solution is an indication of cobalt but should not be taken as a

² McALPINE, R. K. AND B. A. SOULE, "Qualitative chemical analysis," D. Van Nostrand Co. Inc., New York City, 1933, p. 324.

final test. In case a brown coloration is obtained, the quantity of dimethylglyoxime added must be greater—generally 5 ml. is sufficient.

11. *Tests for Cobalt.*—(a) "Vogel's Test." Cover 5 ml. of the solution from (9) with a 1-ml. layer of amyl alcohol. Add 5 ml. of 3 *N* ammonium thiocyanate and shake the solution thoroughly. A blue color, stable in the amyl alcohol layer, is a test for cobalt. It is known that acetone sensitizes this test for cobalt; accordingly the amyl alcohol contains approximately twenty-five per cent. acetone. If a red color develops because of the presence of ferric ions, add stannous chloride solution until this color disappears.

(b) Neutralize another 5 ml. of the solution from (9) with ammonium hydroxide and then make acid with acetic acid. Add about 1 ml. of a saturated solution of alpha-nitroso-beta-naphthol in fifty per cent. acetic acid and warm the solution. A brick-red precipitate is a test for cobalt.

STUDENTS' RESULTS

A record of students' results with the new procedures has been kept for a period of five semesters. During this time 384 unknowns containing the ions of Group III have been dispensed. The data given below are based on the student use of the procedures outlined above with the exception of the test for zinc with 8-hydroxyquinoline. This test, suggested to the authors by Dr. I. M. Kolthoff,³ has only recently been introduced in the student procedures.

In order to offer some comparison with the classical scheme of analysis column five of Table 1 has been reproduced from a study of student results in qualitative analysis previously published by L. I. Gilbertson.⁴

TABLE 1
PERCENTAGE OF IONS CORRECTLY REPORTED

<i>Metal</i>	<i>Number of times given</i>	<i>Number of times reported</i>	<i>Per cent. accuracy, new procedure</i>	<i>Per cent. accuracy, classical procedure</i>
Cobalt	132	130	98.5	93
Iron	122	120	98.4	94
Manganese	113	111	98.2	91
Nickel	119	116	97.5	94
Chromium	70	67	95.7	89
Aluminum	148	139	93.9	84
Zinc	160	146	91.2	79
		Average 96.2		89.1

³ Private communication.

⁴ GILBERTSON, L. I., J. CHEM. EDUC., 13, 483 (1936).

In Table 2 the data for ions reported when not present are recorded. It seemed logical to the authors to take for the percentage basis, the number of times an ion could have been incorrectly reported. Accordingly, the second column contains values of three hundred eighty-four minus *G*, that is, the number of unknowns in which the ion was not present, *G* being the number of times the ion was given as recorded in Table 1.

TABLE 2
IONS REPORTED WHEN NOT PRESENT IN SAMPLES

<i>Metal</i>	<i>384 - G</i>	<i>Number reported but not present</i>	<i>Per cent. error</i>
Chromium	314	1	0.3
Iron	262	3	1.1
Cobalt	252	3	1.2
Manganese	271	5	1.8
Nickel	265	5	1.9
Aluminum	236	11	4.6
Zinc	224	18	8.0
		Average 2.7	

CONCLUSIONS

The data in the foregoing tables seem to indicate that, in the hands of students, the new procedures possess advantages over the classical scheme of analysis. The percentage accuracy with the new procedures is seen to exceed that obtained by conventional methods by seven per cent. In spite of the comparatively small amount of data now available it does not seem logical to the authors to suppose that this increase in accuracy is due to factors other than to the procedures themselves. The compilation of student results with the new scheme of analysis is being continued.

It is to be noted that zinc, the ion missed most frequently, is also the ion reported most frequently when not present. It is the opinion of the authors that this difficulty will be reduced by the introduction of the 8-hydroxy-quinoline test for zinc. A solution containing as much as 80 mg. each of nickel and cobalt, but no zinc, was separated in the usual way with sodium hydroxide, and the filtrate tested for zinc by the procedure outlined for the 8-hydroxy-quinoline test. Such a "blank" failed to give a test for zinc. On the other hand, it was possible to separate 3 mg. of zinc from 80 mg. each of nickel and cobalt and obtain a distinct test by this method.