

QUALITATIVE ANALYSIS—TIN GROUP.

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Numerous complaints from students that their results in the analysis of the tin division were not clear-cut caused the writer to investigate the matter. Two difficulties were found with the method generally employed. The first was in separating the tin group from the copper group, where care in avoiding solution of the latter led to incomplete solution of the former. The second was in separating tin and antimony from arsenic where appreciable amounts of arsenic sulphide dissolved to cause trouble later on.

Since it is generally necessary to remove traces of copper and mercury from the tin group precipitate, it was decided to make the treatment with polysulphide so severe that this procedure would become the rule. This should insure complete separation of the two divisions.

A somewhat similar decision was made in the case of the second part of the problem. It was decided to heat the reprecipitated tin group sulphides with 12N HCl at the temperature of boiling water since it is a simple matter to remove the arsenic sulphide which dissolves.

In order to avoid the difficulty which students have with the use of test-lead in reducing tin, aluminium was substituted for lead with good results.

The method finally adopted is as follows:

Method. Wet the sulphides on the filter with ammonia in an evaporating dish. Add about 15cc. polysulphide and set over a beaker of boiling water for five minutes. During the heating, the dish should be covered with a watch-glass. The contents should be stirred occasionally. Filter and treat the residue a second time with ammonia and polysulphide. Filter into the original filtrate. The residue contains all but a trace of the copper group.

Make the filtrate just acidic with dilute HCl and filter. Transfer the precipitate and paper to a dish and heat over boiling water with about 15cc. 15N ammonia for three to five minutes, adding more ammonia from time to time to replace that which boils off. This treatment dissolves the tin group sulphides. Filter, and wash the residue with warm ammonia. The residue may be added to the copper group precipitate. Acidify the filtrate with 6N HCl, being careful not to add a great excess and filter.

Transfer the paper and precipitate to a large test-tube and add 10cc. 12N HCl. Set the tube in a beaker of boiling water for ten minutes. Cool, filter, and wash the precipitate on the filter with 5cc. cold 6N HCl. Confirm arsenic in the residue.

Add 20cc. water to the filtrate. Unless this dilution causes the precipitation of orange antimony sulphide, pass in hydrogen sulphide until it starts to precipitate or to saturation if it does not appear. If antimony has precipitated, warm until it redissolves and filter. If it is absent, filter. This treatment removes all arsenic.

Boil the filtrate down to about 20cc. and transfer it to a large test-

tube. Add .1-.2g. 30-mesh aluminium. Warm the solution and shake it while the metal is going into solution so as to insure contact of the metal with all parts of the solution. Continue to heat until all gas-evolution has ceased so as to avoid carrying over tin with the precipitated antimony. Let the black antimony settle to the bottom of the tube and decant the liquid through a filter into a tube containing some mercuric chloride solution. A white precipitate, which may turn gray, proves the presence of tin.

Wash the black precipitate in the tube with hot 12N HCl and with water to remove traces of tin. This may be done by decantation. Cover with 3cc. HCl, add a few drops of nitric and boil to destroy the aqua regia. Dilute to about 20cc. and pass in hydrogen sulphide. An orange precipitate proves the presence of antimony.

The writer wishes to thank his student, Mr. Merrell Fenske, for the aid he has given in working out this problem.

QUALITATIVE ANALYSIS—IRON GROUP.

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Careful examination of the results obtained by several classes in Qualitative Analysis has led the writer to the belief that no other group causes so much trouble or consumes so much of the students' time as does the Iron Group. Further study has brought out the fact that the most commonly missed members of this group are cobalt and zinc. The difficulty with the first of these seems to be due to faulty application of the potassium cobaltinitrite test, and with the second, to failure to extract zinc from the group precipitate and the reluctance of the average student to seek for it in the second division precipitate.

Investigation of the various tests for nickel led the writer to attempt a modification of the old Morrel-Vogel test. The results in this direction were quite satisfactory and pointed to the possibility of greatly simplifying the scheme of analysis of the whole division.

Attention was then directed toward the zinc problem. If zinc could be satisfactorily separated from the second division, the necessity for the very annoying and time-consuming second precipitation and filtration of cobalt and nickel sulphides would be avoided. This notwithstanding contrary belief on the part of certain authors, was found to be quite satisfactorily accomplished by using a large excess of sodium hydroxide in separating the two divisions. (It must be noted that this procedure may increase the quantity of silicic acid in solution, though in no case has there been evidence of nickel being present in the zinc sulphide precipitate.) There is no desire on the part of the writer to deny that small quantities of zinc may be carried over in the second group precipitate but he does hold that except in very extraordinary cases it is unnecessary to look for it as the greater part of it will show up in the proper place.

Several other slight deviations from the more commonly accepted methods will be noticed in a study of the revised method which follows. They are all in the direction of speeding up the process without lessening its accuracy.

METHOD OF ANALYSIS.

Dissolve the group precipitate of sulphides and hydroxides (adding the filter if difficult to separate from the precipitate) in warm 6N HCl, adding a few drops of HNO_3 if necessary (if cobalt or nickel is present). If the filter was added, remove the fibers by sucking the solution through a Hirsch funnel. Wet the pulp remaining in the funnel with water and draw the water into the filtrate. Except for particles of sulphur the pulp will be white after this treatment.

Boil the filtrate for a minute and then add 30 per cent NaOH solution until a precipitate forms and persists after shaking or, if no precipitate appears, until solution is strongly alkaline. If there is a precipitate, add a further excess of 5-10cc. NaOH. Cool and add 1-3g. Na_2O_2 a little at a time with stirring. Add about half a gram of solid Na_2CO_3 and boil for a minute or two. Dilute with two volumes of hot water and boil for three minutes. Filter hot through an ordinary filter, the writer using a suction filtration by preference. Wash the precipitate on the filter with hot water, collecting the washings with the filtrate. The filtrate is treated as directed in Noyes' "Qualitative Analysis" for the separation of the first division metals.

The paper carrying the precipitate is spread out in a dish and covered with 15cc. boiling 6N HNO_3 . This treatment dissolves or loosens the precipitate from the paper so that it can be transferred to a beaker. The paper is washed with another portion of hot acid and the solution added to the other. The solution is evaporated to 10cc. and 10cc. 16N HNO_3 added. The boiling solution or suspension, as the case may be, is removed from the flame and about a gram of KClO_3 is added with stirring. This produces complete precipitation of the manganese as the oxide unless there is a very large quantity of it present. Twenty cc. hot water is added, the solution or suspension boiled and filtered hot through an ordinary filter. Oxalates, if present, slow up the precipitation of the manganese and sometimes necessitate a second evaporation and addition of chlorate.

The filtrate contains iron, cobalt, and nickel, and fourth group ions if phosphates, oxalates, etc. are present. When these interfering ions are absent, add quickly with stirring a volume of 15N NH_4OH 5cc. in excess of the volume of HNO_3 present. If iron is present it will appear as the brown hydroxide. Quickly heat almost to boiling and filter hot. Wash the precipitate on the filter with 2-5cc. NH_4OH , collecting it with the original filtrate. Confirm iron in the precipitate.

In a tall 150cc. beaker boil off the ammonia from the filtrate until its odor is weak but noticeable. Pour off about one-fifth of the solution and test for nickel by adding a few drops of dimethylglyoxime solution. If nickel is present, a red precipitate will form at once. It is never necessary to correct for hydrogen ion concentration in this test if the above directions are closely followed.

Evaporate the remainder of the solution to a syrupy consistency and pour it into a test tube. Cool, and add enough water to bring most of the solid into solution. The reaction at this point is acidic. Add 3cc. 10 per cent KCNS solution and then 2.5cc. amyl alcohol-ether

solution (1 vol.: 3 vol.). For convenience in the laboratory these solutions may be kept in bottles fitted with bulb tubes so marked that the correct volumes may be withdrawn and added to the solution to be tested. Shake gently. If cobalt is present the upper layer will have a distinct blue-green color. If the color is not distinct carefully add a few drops of 12N HCl to the ether layer. Presence of cobalt produces the blue color. A colorless or straw-colored layer indicates its absence. This test can be applied in most cases to the original solution if iron is absent.

When oxalates or phosphates are present, they may be removed in the usual way by precipitating the iron, cobalt, and nickel as the sulphides after removing the manganese and treating the precipitate.

RESULTS.

The following mixtures gave good, clear-cut tests for all of the metals shown. The numbers represent milligrams of the atom named.

	Zn	Cr	Mn	Fe	Co	Ni	Al
1.....	—	—	9	9	1.8	9	—
2.....	—	—	3.6	3.6	3.6	18	—
3.....	—	—	1.3	13.3	.7	13.3	—
4.....	—	—	2	100	1	100	—
5.....	.5	—	—	250	—	—	—
6.....	.5	—	250	—	—	—	—
7.....	.5	—	250	250	—	—	—
8.....	.5	—	500	500	—	—	—
9.....	.5	—	500	500	2	3	—
11.....	.5	8.5	500	500	2	3	—
12.....	.5	—	1	—	.5	.5	—
13.....	.5	17	18	20	10	.5	—
14.....	2	—	500	500	1	10	—
15.....	10	—	100	100	2	100	100

SUMMARY.

A simplified scheme for the analysis of the Iron Group has been worked out which takes less time and appears to give more consistent results than the methods generally used.

The troublesome reprecipitation of cobalt and nickel as the sulphides and the careful adjustment of the reaction of the solution for the dimethylglyoxime test for nickel have been eliminated.

The Morrel-Vogel test for cobalt has been improved.

A table showing the wide range of application of the scheme described is given.

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