Table VII.—Vol. 50 cc., 2 grams NH_4Cl.

Minimum amounts of metal which gave a precipitate when the solution was rendered alkalin with ammonia:

	10 mg. PO_4.[1]	25 mg. PO_4.	100 mg. PO_4.
Ba	25	20	10
Sr	12	8	5
Ca	1	..	..
Mg	1	..	..

Comments on Table VII.—With Ba and Sr, 1 mg. of the metal gave a very faint cloudiness, but it was only with the quantities noted in the table that a definit precipitate was obtained; however, 1 mg. of Ca and Mg was in each case sufficient to yield a distinct precipitate. Experiments with larger amounts of ammonium chloride gave the same results noted in the table.

Summary.

The effect of a number of non-volatil organic substances to prevent or hinder the precipitation of aluminium, chromium, and iron by NH_4OH was investigated. The following was found to be the order of interference: Citric acid, tartaric acid, dextrin, sucrose, glucose and lactose. The first offered the greatest interference, while sucrose, glucose and lactose interfered very slightly in the precipitation of the trivalent metals of Group III. Tables are given showing the effect of each of the above substances under conditions which prevail in qualitative work. A study was also made of the influence of certain acids in causing the precipitation of the alkalin earth metals and magnesium, in the third group. It was found that 2 grams of ammonium chloride, which are formed in the course of the analysis, are sufficient to prevent any interference by boric acid or borates; with fluorides, however, this was not found to be the case, even when the amount of ammonium chloride was increased. The effect of varying quantities of oxalates and phosphates, respectively, on the precipitation of barium, strontium, calcium and magnesium in the third group, was also investigated.

[Contribution from the Laboratory of Analytical Chemistry, College of the City of New York.]

A METHOD FOR THE SYSTEMATIC QUALITATIVE DETECTION OF BARIUM AND STRONTIUM.[2]

By Louis J. Curtman and Edward M. Frankel.

Received September 18, 1912.

The recent work of the authors[3] conclusively demonstrated that the

---

[1] For experiments with smaller amounts of phosphate see Noyes, Bray and Spear, This Journal, 30, 534.

[2] Published in abstract in the original communications of the Eighth Internationa Congress of Applied Chemistry, Vol. 1, p. 151.

[3] This Journal, 33, 724 (1911).

present method of detecting small amounts of barium (even up to 50 mg.) in systematic qualitative analysis is unreliable. What was found to be true for barium is probably true for strontium too, though, to be sure, in a lesser degree. The need for modification of the old scheme of analysis is therefore evident. The authors know of no method for remedying this difficulty other than to precipitate the alkalin earth elements as sulfates before the separation of the heavy metals with hydrogen and ammonium sulfides.[1] In this connection it is of interest to note the work of Browning and Blumenthal[2], in which these authors propose a method which consists in the precipitation of the alkalin earth sulfates from the filtrate of the silver group by the use of a 10% ammonium sulfate solution in the presence of ammonium acetate, the latter reagent being employed to prevent the simultaneous precipitation of lead sulfate. Their work, however, is open to objection, mainly because of their failure to adhere in their preliminary work, to the conditions that are actually prevalent in systematic analysis. A little work on the part of the authors has shown that strict adherence to these conditions is necessary because of the variation in results otherwise obtained. It was with the object of devising a method which would remove the alkalin earths prior to the precipitation of the heavy metals with hydrogen sulfide and of making the method universally applicable, that the present work was undertaken.

The chief considerations which must be taken cognizance of, in order that the method proposed should be applicable in all cases are:

1. Volume and Acidity of Solution.—The volume of the filtrate from the silver group precipitation is generally 25 cc., hence this volume was adopted in this work. In order that uniform results be obtained, it is necessary that the acidity of the solution be kept constant. However, as solutions submitted for analysis generally have an unknown acidity (HCl or HNO_3), definit provision must be made for its adjustment. In any case the acidity must be above a given minimum value in order that 500 mg. of antimony or bismuth may be held in solution. The method consists in neutralizing the free acid with ammonia and then adding a definit quantity of hydrochloric acid.[3]

2. Influence of Ammonium Salts.—The ammonium salts introduced by the neutralization of the free acid have the effect of decreasing the sensitiveness of the reaction, as may be noted from the table below.

3. Choice of Reagent.—As ammonium sulfate and sulfuric acid recom-

---

[1] It may be of interest to state that the precipitation of barium strontium and calcium after the removal of the silver group was used by Professor Hinrichs in a qualitative analysis published in Iowa in 1876.—EDITOR.

[2] *Am. J. Sci.*, **32**, 246 (1911).

[3] Experiments made to determin how much acid is necessary to hold 500 mg. of bismuth or antimony in solution showed that 2.5 and 5.0 cc. HCl (sp. gr. 1.2), respectively, were necessary.

mend themselves for precipitants, it was found desirable to determin by experiment the more suitable of the two. The solutions were of such strength that from 5–10 cc. of reagent would be more than enough to effect complete precipitation of 500 mg. of any of the alkalin earth elements. The solutions used were 20% sulfuric acid (8 cc.) and 40% ammonium sulfate (5 cc.).

4. Use of Alcohol to Complete Precipitation.—Preliminary experiments carried out under the adopted conditions of volume and acidity, showed that the precipitation of the alkalin earth sulfates was hastened and rendered more complete by the addition of alcohol.[1] The results of these experiments are summarized in the table below:

TABLE I.—LEAST AMOUNTS (MILLIGRAMS) DETECTED. VOLUME 25 CC. ACIDITY 5 CC. HCl (SP. GR. 1.19). EQUAL VOLUME OF 95% ETHYL ALCOHOL ADDED AFTER PRECIPITATION. SOLUTIONS OBSERVED AFTER FIVE MINUTES.

	8 cc. 20% H_2SO_4.			5 cc. 40% $(NH_4)_2SO_4$.		
	No alcohol.	Alcohol.	Alcohol + 5 g. NH_4NO_3.	No alcohol.	Alcohol.	Alcohol + 5 g. NH_4NO_3.
Ba	0.5	0.5	0.5	0.5	0.5	0.5
Sr	5.0	0.5–1.0	1.0–1.5	10.0	0.5–1.0	2.0
Ca	100.0	7.0	10–12	100.0	7.0	10–12
Pb	50.0	15.0	10–12	50.0	12.0	20–25

An examination of the above table shows that under definit conditions of acidity, the use of dilute sulfuric acid and alcohol affords an easy method for the complete separation of even small amounts of barium and strontium. The failure of the method to detect small amounts of calcium and lead does not militate against it, for the reason that these elements, in small amounts, are readily detected at other points of the analysis. Indeed, we may turn this apparent objection into an advantage inasmuch as we can utilize this failure to yield a precipitate for the purpose of semi-quantitative estimation. The failure to detect calcium or lead at this point would prove that no more than 10–12 mg. of either element was present.

The alcohol introduced into the solution may be readily removed by boiling down the filtrate to about half its bulk, care being taken that the solution is continuously stirred to prevent mechanical loss due to bumping.[2]

---

[1] In this connection, it may be well to mention the fact, that the ordinary 95% alcohol was found unsuitable for this work, for the reason that it gave a distinct cloudiness on dilution with water or with dilute acid. However, by redistilling it, a product was obtained which gave perfectly satisfactory blanks. The residual liquid in the distilling flask was slightly yellow, and on further concentration yielded a mass of long needles, which were found to be difficultly soluble in alcohol and insoluble in water; it was this substance which was undoubtedly responsible for the unusual behavior of the alcohol on dilution. This experience of ours would indicate the necessity of testing the alcohol with water before using it in this work.

[2] It was feared that, on removing the alcohol by boiling, some arsenic would be volatilized. Experiments, however, showed that small amounts (2 mg.) could be readily detected after boiling out the alcohol.

The method adopted as a result of the experiments and consideration mentioned above is as follows:

The filtrate from the precipitation of the silver group is just neutralized with ammonia and the solution reacidified with 5 cc. of concentrated hydrochloric acid. Eight cubic centimeters of 20% sulfuric acid are then added and the solution boiled. It is then allowed to cool and an equal volume of 95% alcohol added. The precipitate is then allowed to settle and the clear liquid decanted off through an ashless filter.[1] The precipitate is then washed once by decantation, keeping as much of it as possible in the beaker. The filtrate is boiled with constant stirring to drive off the alcohol and is reserved for further analysis. The precipitate of washed sulfates is then treated with a hot solution of ammonium acetate until the extract no longer gives a test for lead with sulfuric acid. The precipitate is then boiled with a 20% solution of sodium carbonate to convert the sulfates to carbonates. The residue, after thorough washing to remove sulfates, is dissolved in acetic acid. Should the solution in acetic acid be incomplete, the residue that remains should be treated with sodium carbonate as before, and the acetic acid solution of the residue combined with the original solution of the carbonates. The solution of alkalin earth acetates is then analyzed for the individual elements by the method proposed by Bray.[2]

The above method was tested out for us by Mr. Rudolph Kramer who had no previous experience with the method. All solutions were submitted to him as unknowns and their composition was such as to insure the thorough testing of the method.

TABLE II.—TEST ANALYSES.

Solution.	Ba.	Sr.	Ca.	Pb.
A.	500	...	...	...
B.	500	2	...	...
C.	1	500	...	...
D.	1	2	500	...
E.	1	300	100	100
F.	1	5	15	...
G.	5	2	20	50
H.	500	1	...	...
I.	1	...	2	25
J.	1	250	15	30
K.	250	1	250	...
L.	250	5	...	...
M.	1	1	250	...

The results of the above analyses were all satisfactory; however, in one

---

[1] An ashless filter was preferred for the reason that a clear filtrate was at once obtained, while with the ordinary qualitative filter paper a second filtration was frequently required.

[2] Bray, THIS JOURNAL, **31**, 615–9 (1909).

or two cases where 1 mg. of strontium was present, the tests were faint, but conclusive.

Summary.

The previous work of the authors[1] has shown that the systematic qualitative detection of barium is distinctly unreliable. They have devised a scheme of analysis by which small amounts of the alkalin earth metals may be detected. The method consists in the precipitation of the alkalin earth metals together with part of the lead as sulfates, with dilute sulfuric acid and alcohol, from a solution of definit acidity. After extracting the lead sulfate with ammonium acetate, the alkalin earth sulfates are converted to carbonates by boiling with sodium carbonate solution. The carbonates are then dissolved in acetic acid and the resulting solution analyzed in the usual manner. Numerous test analyses prove the method to be trustworthy.

POTASSIUM AMMONOTITANATE—N≡Ti-NHK.[2]

By Edward C. Franklin and Thomas B. Hine.

Received August 30, 1912.

In a paper on the ammonia system of acids, bases and salts,[3] the senior author has shown that the amides and imides and the nitrides of the non-metallic elements are to be looked upon respectively as ammono acids and acid ammonides, which may be expected to react with ammono bases in liquid ammonia solution to form ammono salts in a manner analogous to the action of aqueous potassium hydroxide on the hydroxides and oxides of the non-metallic elements.

In order to test this view experimentally, one of us (F.) prepared silicon amide[4] by the ammonolysis of silicon tetrabromide and subjected it to agitation in contact with excess of potassium amide in liquid ammonium solution, with the result that a product was obtained roughly approximating the composition represented by the formula N≡Si–NHK. The unsatisfactory results of this experiment, but more especially the prospect

---

[1] *Loc. cit.*

[2] The experimental work here described was carried out by the junior author in the chemical laboratories of the Leland Stanford Junior University during the academic year 1910–11 and was incorporated in a thesis submitted in partial fulfilment of the requirements for the degree of Master of Arts. The publication of the rather unsatisfactory results obtained has been delayed in the hope that the opportunity would present itself for a continuation of the investigation. The appearance of a recent paper by Ruff and Treidel [*Ber.*, **45**, 1364 (1912)] in which certain of Hine's results are anticipated [cf., however, *Am. Chem. J.*, **47**, 306 (1912)] renders further delay in publication inadvisable.

[3] *Am. Chem. J.*, **47**, 298 (1912).

[4] Lengfeld, *Ibid.*, **21**, 531 (1899); Vigouroux and Hugot, *Compt. rend.*, **136**, 1670 (1903).