properties of this acid. It is neither poisonous nor explosive and is perfectly stable (unlike the anhydrous acid). It is, as a rule, non-oxidizing except near its boiling point, 203°, and by reason of the latter being so high, it is capable of displacing completely from their salts, nitric, hydrofluoric, hydrochloric and other volatil acids. Most of its salts are readily soluble not only in water, but also in organic solvents like alcohol and acetone, and they are very suitable for electrochemical work, since they suffer no reduction by electrolysis. Its principal use in the laboratory is in the separation of potassium and sodium, but other uses will suggest themselves when it becomes cheaper. Andrews[1] has suggested it as a solvent for barium chromate in the volumetric determination of sulfur. It is very suitable for use in electrolytic analyses.[2] It makes an excellent standard solution for use in acidimetry where a non-volatil acid is required and sulfuric is not suitable. It may be substituted for sulfuric acid in permanganate titrations; the evaporation of ferric chloride solutions with perchloric acid to complete removal of chloride is not attended with the formation of difficultly soluble basic salts, as frequently occurs with sulfuric acid, and the addition of a little water causes immediate solution of the residue. In technical work, its extended use seems already assured, especially in electrochemical processes, judging from the number of such patents issued.

Summary.

1. A method is given for preparing pure $HClO_4.2H_2O$ from ammonium perchlorate by boiling with the proper quantity of dilute nitric acid, to which a certain amount of hydrochloric acid is gradually added.

2. The principal gaseous products are nitrous oxide and chlorine.

3. The superiority of this process lies in its simplicity, rapidity, and the cheapness of materials.

4. The distillation of the acid is briefly described.

5. Some of its most striking properties and a few new uses for it are mentioned.

ANN ARBOR, MICH.

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THE INFLUENCE OF NON-VOLATIL ORGANIC MATTER AND CERTAIN ACIDS ON THE PRECIPITATION OF THE AMMONIUM SULFIDE GROUP OF METALS.[3]

BY LOUIS J. CURTMAN AND HARRY DUBIN.

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As is well known, there are two classes of substances whose presence

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[1] *Am. Chem. J.*, 32, 476.

[2] THIS JOURNAL, 34, 389; *Trans. Am. Electrochem. Soc.*, 9, 375.

[3] Published in abstract in the original communications of the Eighth International Congress of Applied Chemistry, Vol. 1, p. 153.

calls for a modified procedure in the analysis of the ammonium sulfide group. The first includes the various forms of non-volatil organic matter, the effect of which is to prevent or hinder the precipitation of the trivalent metals, iron, chromium, and aluminium by ammonia; the other class comprises those acids whose barium, strontium, calcium, and magnesium salts are insoluble in water, and in slightly ammoniacal solutions and are hence precipitated along with the metals of the third group, when the filtrate from the hydrogen sulfide group is rendered alkalin with ammonia. These acids are phosphoric, hydrofluoric, silicic, oxalic and boric.

In most schemes of analysis, silicic acid is usually removed at the outset of the work; at any rate, its removal is easily accomplished and hence it has not been considered in this work.

Beyond the general statement to be found in all the text books, that the above mentioned substances interfere, as well as some experiments by Noyes, Bray and Spear,[1] there appears to be no record of any systematic work performed with a view to determin, precisely, the extent of these interfering substances under the conditions which prevail in qualitative analysis.

It was, therefore, the object of this investigation to carry out a series of experiments for the purpose of supplying these data, on the basis of which a rational modified procedure may be devised.

1. Influence of Non-volatil Organic Matter.

For these experiments, those substances which are most commonly met with in mixtures submitted for qualitative analysis were employed, *viz.*, tartaric acid, citric acid, sucrose, lactose, glucose, and dextrin. As the results of this work were to be of special significance when applied to schemes of qualitative analysis, it was thought necessary in the experiments which follow, to keep the conditions the same as those which prevail in qualitative work. Accordingly, the total volume of the solution in each experiment, except where otherwise mentioned, was kept at 50 cc., this being, in our opinion, the proper volume to which the filtrate from the second group precipitate should be evaporated, before precipitating the metals of group three.

The general procedure was as follows: To separate solutions containing a fixed amount (50 mg.) of the non-volatil organic matter whose interfering influence was to be determined, was added a definit quantity of one of the trivalent metals in the form of a solution of one of its salts; the solution was then diluted to 50 cc., heated to boiling, and finally treated with a slight excess of 10% ammonia. If no precipitate formed, the experiment was repeated a number of times with increasing amounts of the same metal, until a precipitate was formed on rendering the solution slightly alkalin with ammonia. In each test, the solution was

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[1] THIS JOURNAL, 30, 534.

examined for a precipitate at the time of adding the ammonia, and again at the expiration of five minutes. The salts employed throughout this work were $FeCl_3.6H_2O$, $Cr(NO_3)_3.9H_2O$, and $AlCl_3.6H_2O$; the results, however, were calculated in terms of the metal.

A. Tartaric Acid.—With this substance, the results obtained are given in Table I below:

Table I.—Vol. 50 cc., 50 mg. $H_2C_4H_4O_6$.

Minimum amount that will yield a ppt. when the solution is rendered alkalin with NH_4OH:

Fe, 55 mg.; Cr, 70 mg.; Al, 20 mg.

Comments on Table I.—With solutions of ferric chloride, a slight yellowish cloudiness was obtained in each test on heating the solution to boiling, before adding the ammonia, due to the hydrolysis of ferric tartrate. The solution was cleared with the addition of a few drops of hydrochloric acid, before treating with ammonia.

When quantities of metal less than the minimum given in the table were used, the final results were characteristic cloudy solutions which could not be cleared by filtering through an S & S No. 595 filter, and which failed to coagulate on prolonged boiling. It is also worthy of note that, when the precipitates obtained with the minimum amounts of each of the trivalent metals were filtered off, cloudy filtrates were obtained in each case. The same was noted in the experiments with citric acid.

Experiments were also carried out to determin whether or not there is a direct proportionality existing between the amount of metal prevented from precipitating, and the quantity of tartaric acid present, when the volume is kept constant. The results obtained were as follows: with 100 mg. of tartaric acid, the minimum amounts of metal that would yield a precipitate were Fe, 130 mg.; Cr, 150 mg.; Al, 45 mg.; showing that the amounts of metal prevented from precipitating by ammonia are roughly proportional to the quantity of tartaric acid present.

B. Citric Acid.—In Table II are given the results obtained with this acid:

Table II.—Vol. 50 cc., 50 mg. $C_6H_8O_7.H_2O$.

Minimum amount that will yield a precipitate when the solution is made alkalin with NH_4OH:

Fe, 70 mg.; Cr, 90 mg.; Al, 40 mg.

Comments on Table II.—With 50 mg. of iron, a yellowish cloudiness was obtained on heating the solution to boiling before adding the ammonia, due to the hydrolysis of ferric citrate. The solution was cleared with the addition of a few drops of hydrochloric acid, before adding the ammonia, as was done in the case of tartaric acid.

Experiments with less than the minimum amounts of metal noted in the table gave, for the final results, characteristic cloudy solutions which could not be cleared by filtering through an S & S No. 595 filter and which did not coagulate on prolonged boiling. As with tartaric acid, experiments were here likewise made to determin whether or not the quantity of metal prevented from precipitating was proportional to the amount of citric acid present, with results which indicated that this was the case. Comparison of the corresponding figures in Tables I and II shows that citric acid offers more interference than does tartaric acid.

C. Sucrose.—The results obtained with this substance are given below in Table III:

Table III.—Vol. 50 cc., 50 mg. $C_{12}H_{22}O_{11}$.

Amount necessary to produce a ppt. when the solution is made alkalin with NH_4OH:

Fe, 1 mg.; Cr, 3 mg.; Al, 2 mg.

Comments on Table III.—Solutions containing 1 mg. of Cr and Al, respectively, also give a precipitate, but only on boiling down the solution to about 20 cc.

To determin whether or not larger amounts of sucrose would have a greater interference, experiments were made with 100 mg. of this substance. The results showed that 2 mg. of Fe, 2 mg. of Al and 4 mg. of Cr were each sufficient to yield a precipitate.

In this connection it may be mentioned that the minimum quantity of metal needed to give a precipitate is influenced by the amount of ammonia used, as is shown by the following results:

TABLE IV.—100 MG. SUCROSE, VOL. 50 CC. HEATED TO BOILING AND THEN RENDERED ALKALIN WITH NH_4OH.

Fe.	NH_4OH.	Result.	Al.	NH_4OH.	Result.
2 mg....	0.2 cc.	Ppt. within 1 min.	2 mg.	0.5 cc.	Ppt. after 1 min.
2 mg....	0.5 cc.	Ppt. within 1 min.	2 mg.	1.0 cc.	Ppt. after 2 min.
2 mg....	1.0 cc.	No precipitate	2 mg.	2.0 cc.	No precipitate
3 mg....	0.2 cc.	Immediate precipitate			
3 mg....	0.5 cc.	Ppt. after 1 min.			
3 mg....	1.0 cc.	Ppt. after 2 min.			
3 mg....	2.0 cc.	No precipitate			

It is to be noted, however, that 1 mg. of each of the metals was sufficient to cause a cloudiness when the solutions were rendered slightly alkalin with ammonia; also, that a precipitate was obtained in each case when the solution was boiled down to about 20 cc., due to the fact that the excess of ammonia was boiled off.

From these results, it appears that sucrose offers very little interference.

D and *E. Lactose and Glucose.*—Experiments carried out with each of these substances in varying amounts, gave substantially the same results as those noted under sucrose; they offer practically no interference.

F. Dextrin.—In Table V below, are given the results obtained with this substance:

Table V.—Vol. 50 cc., 50 mg. dextrin.

Amount necessary to produce a precipitate when the solution is made alkalin with NH_4OH:

Fe, 17 mg.; Cr, 12 mg.; Al, 1 mg.

Comments on Table V.—With 50 mg. of dextrin, 1 mg. of iron gave a precipitate only when the solution was boiled down to about 10 cc. With amounts of chromium less than 12 mg., a cloudiness was obtained which did not coagulate on prolonged boiling. Experiments with larger amounts of dextrin than those given in the table showed that, with 350 mg. of the substance, a cloudiness was obtained with 1 mg. of iron and aluminum, respectively, but it was only when the solutions were concentrated by boiling down to about 20 cc. that a precipitate was obtained. With 100 mg. of dextrin, 20 mg. of chromium were required to yield a precipitate. Below 20 mg. of the metal, a cloudiness was obtained which did not coagulate on boiling.

2. Influence of Acids.

It is the purpose of the following experiments to establish:

(1) The effect of borates, oxalates, phosphates and fluorides, in causing the precipitation of barium, calcium, strontium and magnesium, in the third group, under conditions that prevail in a systematic qualitative analysis, *i. e.*, in a volume of 50 cc., in the presence of varying amounts of ammonium chloride, and a slight excess of ammonia.

(2) Whether ammonium chloride exercises any influence in preventing the precipitation of the above named metals, and, if so, whether there is any relation between the amount of this salt present and the quantities of metal that are prevented from precipitating.

The general procedure was as follows: Separate solutions containing from 100 to 1000 mg. of the substance, whose interfering influence was to be studied, were treated, in separate experiments, with from 2 to 10 grams of ammonium chloride, and varying amounts of barium, calcium, strontium, and magnesium; the solutions were then diluted to 50 cc., heated to boiling, and a slight excess of 10% ammonia added. In each experiment, the amounts of interfering substance and of ammonium chloride were kept constant while the quantity of metal added was varied, to find the minimum amount that would yield a precipitate under these conditions. The maximum amount of metal used in any case was 500 mg.; beyond this quantity of metal it was thought unnecessary to work. In each experiment, the solution, after the addition of ammonia, was examined for a precipitate, allowed to stand for five minutes, and then re-examined. The salts used in this work were $BaCl_2.2H_2O$, $CaCl_2$,

$SrCl_2.6H_2O$, and $MgCl_2.6H_2O$; but the results were calculated in terms of the metal.

A. (*a*) *Borates, as* H_3BO_3.—Experiments with increasing amounts of this substance up to 1000 mg. in the presence of 2 grams[1] of ammonium chloride showed that in no case was a precipitate obtained with barium, strontium, and magnesium, even when 500 mg. of metal were used. These results indicate that 2 grams of ammonium chloride are sufficient to prevent as much as 500 mg. of metal from precipitating in a slightly alkalin solution containing as high as 1000 mg. of borate.[2] This condition of slight alkalinity applies throughout this work.[3]

The same results were obtained with calcium when increasing amounts of borate up to 500 mg. were used. When, however, 1000 mg. of borate was present, a precipitate was obtained with 500 mg. of calcium. When the last experiment was repeated with 4 grams of ammonium chloride no precipitate was obtained. From these results it is evident that 2 grams of ammonium chloride must be added, to keep the same amount of calcium in solution.

To determin the separate effects of dilution and absence of ammonium chloride on the precipitation of the borates of barium, calcium, strontium, and magnesium, the following tests were made: Separate solutions, containing 100 mg. of borate as boric acid, and only 2 mg. of barium, calcium, strontium, and magnesium, respectively, were treated with a slight excess of ammonia, with the result that immediate precipitates were obtained, which dissolved on adding ammonium chloride or on diluting to 50 cc.

Separate solutions, containing 1000 mg. of borate and 500 mg. of each of the above metals, were diluted to 50 cc. and treated with a slight excess of ammonia. Immediate precipitates were obtained in all cases.

(*b*) *Borates, in the form of* $Na_2B_4O_7$.[4]—Substantially the same results were obtained with this substance for barium, strontium and magnesium, as we have recorded above for boric acid.

Calcium gave the same results when the quantity of borate did not exceed 250 mg. If, however, 500 mg. of borate were employed, then, in the presence of 2 grams of ammonium chloride, a precipitate was obtained with about 250 mg. of calcium. If, now, 4 grams of ammonium

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[1] This quantity was used because it is the minimum amount of ammonium chloride that is formed in consequence of the neutralization of the free hydrochloric acid from the second group.

[2] These results are a confirmation and extension of the work of Noyes, Bray and Spear, THIS JOURNAL, 30, 534.

[3] When a large excess of ammonia was used under the same conditions, a precipitate was obtained, hence the importance of avoiding a large excess of ammonia.

[4] The maximum amount of borate used was only 500 mg., as we were limited by the solubility of borax.

chloride were used, then no precipitate was obtained on the addition of even 500 mg. of calcium, showing that 4 grams of ammonium chloride were sufficient to prevent 500 mg. of calcium from precipitating in the presence of 500 mg. of borate.

B. Fluorides as NH_4F.—With this substance, the following experiments were carried out:

(*a*) A solution, containing 10 mg. fluorine as ammonium fluoride, 2 grams of ammonium chloride and 1 mg. of calcium, was diluted to 50 cc., heated to boiling and treated with a slight excess of ammonia. The result was a very finely divided precipitate that gave the solution a cloudy appearance.

(*b*) The same experiment was repeated with 4 grams of NH_4Cl with the same result.

(*c*) Separate solutions, containing 10 mg. of fluorine as NH_4F, 2 grams of NH_4Cl and 1 mg. of Ba, Sr and Mg, respectively, were diluted to 50 cc., heated to boiling, and treated with a slight excess of ammonia. In each case such a small quantity of an extremely finely divided precipitate was obtained that it could not be seen except when viewed against a black and white background. On increasing the amount of metal, the size of the precipitate increased slightly, but there was no definit point below which it might be said that no precipitate was obtained.

(*d*) The same results were obtained when the experiments were repeated with 4 grams of ammonium chloride.

(*e*) Separate solutions, containing 100 mg. fluorine as NH_4F, 2 grams of ammonium chloride, and 1 mg. of Ba, Ca, Sr, and Mg, respectively, were diluted to 50 cc., heated to boiling, and treated with a slight excess of ammonia, with the result that a precipitate was obtained in each case. Increasing the amount of ammonium chloride had no effect on the results, showing that, contrary to the statements which appear in most books, ammonium chloride does not prevent the precipitation of these metals by ammonia in the presence of fluorides.

Experiments carried out with NaF gave the same results as those obtained with the ammonium salt.

The following experiments were also performed:

1. Separate solutions, containing 50 mg. F, as NH_4F, 100 mg. Fe, as $FeCl_3$, 4 grams NH_4Cl, and 75 mg. Ba, 50 mg. Sr, 20 mg. Ca, 15 mg. Mg,[1] respectively, were diluted to 50 cc., heated to boiling, treated with a slight excess of ammonia, and filtered. The filtrates tested for the above metals with suitable reagents[2] gave precipitates with Ba and Sr, none in the case of Ca, and but a very faint cloud with Mg.

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[1] These amounts of metal were employed in order that the 50 mg. of fluorine used would supply an excess of precipitant.

[2] The test for Mg was made with Na_2HPO_4, for Ba with dilute H_2SO_4, for Ca with $(NH_4)_2C_2O_4$, and for Sr with dilute H_2SO_4 and $CaSO_4$ solution.

Blank tests carried out in the absence of fluorine gave precipitates in each case.

2. Experiment 1 was repeated with 15 mg. of Ba and Sr, respectively, with the result that precipitates were obtained in both cases.

C. Oxalates in the form of $H_2C_2O_4$.—Experiments carried out with variable amounts of oxalate gave the results tabulated below.

Table VI.—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. C_2O_4.	25 mg. C_2O_4.	100 mg. C_2O_4.
Ba	60	30	10
Sr	15	2	1
Ca	1	1	1

As the formation of a precipitate on the addition of ammonia may have resulted from the small amount of ammonium carbonate that is always present in the ammonia, blank tests were run side by side, with the above experiments. In no case was a precipitate formed in the blank tests.

With magnesium the following experiments were carried out:

(*a*) A solution containing 250 mg. of oxalate and 2 grams ammonium chloride[1] was diluted to 50 cc., rendered alkalin with about 4 cc. of 10% ammonia and heated to boiling. After standing five minutes a slight cloudiness was observed, although no magnesium had been added.

(*b*) The above experiment was repeated with the addition of 50 mg. of magnesium; the result was a more pronounced cloudiness than that obtained in the blank test.

(*c*) The experiment was repeated with the addition of 200 mg. of magnesium, which gave for the final result a slight precipitate. Comparison of the results obtained in the above three experiments, shows that with 250 mg. of oxalate, it is not possible to determin the minimum amount of magnesium that will yield a precipitate, for the reason that a cloudy solution is obtained as a final result in the blank. Experiment (*a*) was now repeated with 200 mg. of oxalate; the final solution was clear. To determin the minimum amount of magnesium which would yield a precipitate under the conditions of the last test, increasing amounts of magnesium were used. With 20 mg. a very faint cloudiness was produced, while with 30 mg. a slight precipitate was obtained.

D. Phosphates as $Na_2HPO_4.12H_2O$.—Experiments carried out with this substance on barium, strontium, calcium, and magnesium, respectively, gave results that are noted in the table below:

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[1] At this point a slight precipitate of ammonium oxalate was obtained. The quantity of precipitate increased on the addition of ammonia, but dissolved on heating.

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.

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

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[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).