The concordance of the results with each fraction is satisfactory. It is interesting to note that with the uncorrected results a perceptible difference exists between the head and tail of the series and that this difference largely disappears when corrections are applied for rare earth impurity. The uncorrected results with the purest fractions and the corrected result with all the fractions differ very little from Baxter and Chapin's earlier result, 144.275 (Ag = 107.880).

In the preceding table the ratio of silver used to silver chloride obtained in the same experiment is given for all complete pairs of analyses. Since the average ratio is essentially identical with that found by Richards and Wells,[1] 0.752634, it can reasonably be concluded that errors from occlusion by the silver chloride, or from loss of silver chloride, are absent. This is in accord with earlier experience of the same kind.

Summary.

Neodymium nitrate was purified by fractional crystallization of the nitrate from concentrated nitric acid. Chloride, prepared from the final fractions of nitrate, was analyzed by comparison with silver. The atomic weight of neodymium was thus found to be 144.261. The average of this result and that found earlier by Baxter and Chapin, 144.275, is 144.268. The rounded-off figure 144.27 (Ag = 107.88) seems to represent fairly the final outcome of both researches.

We are very greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance, as well as to Dr. H. S. Miner, of the Welsbach Light Company, for the neodymium material.

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THE SOLUBILITIES OF THE SULFATES OF BARIUM, STRONTIUM, CALCIUM AND LEAD IN AMMONIUM ACETATE SOLUTIONS AT 25° AND A CRITICISM OF THE PRESENT METHODS FOR THE SEPARATION OF THESE SUBSTANCES BY MEANS OF AMMONIUM ACETATE SOLUTIONS.

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In the last few years several attempts have been made to separate lead sulfate from the other sulfates which are relatively insoluble in water by the use of ammonium acetate solution. Such a method, where lead sulfate could be completely separated from the sulfates of barium, strontium and calcium, would be of value both in qualitative and quantitative analysis.

Qualitative statements of the solubilities of the four sulfates occur frequently in chemical literature. In the case of lead sulfate it is the general

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[1] *Publ. Carnegie Inst.*, No. 28, 1905; THIS JOURNAL, 28, 456 (1908).

consensus of opinion that it dissolves to a considerable extent in ammonium acetate solutions. Bolley[1] gives the solubility at 12.5° as 1 part in 47 parts of ammonium acetate of specific gravity 1.036 (about 16% solution). Noyes and Whitcomb[2] have given the solubilities of lead sulfate in dilute solutions of ammonium acetate at 25° and Dunnington and Long[3] have published the solubilities of lead sulfate in fairly concentrated solutions at 100°.

According to Storer, calcium sulfate is soluble to a very considerable extent in an aqueous solution of acetate of ammonium at 18–25° and is quite soluble in solutions of other ammonium salts. Cameron and Brown[4] have found that the solubility of calcium sulfate is greater in ammonium nitrate and ammonium chloride solutions than in pure water. As far back as 1823[5] at least, the solubility of strontium sulfate was in dispute. A method for the separation of the sulfate of strontium from that of barium was based upon the solubilities of the sulfates in water. Smithson found, however, that he could get no precipitate with sodium carbonate in the filtrate from a water solution of sodium sulfate in which the sulfate of strontium had lain long. Most of the early authors considered strontium sulfate completely insoluble in solutions of ammonium salts, but at the same time admitted that the ammonium salts of the organic acids interfere with its precipitation. According to Storer, also, the sulfate of barium is soluble to a considerable extent in aqueous solutions of certain ammonium salts. He also states that the precipitation of barium sulfate is prevented by the presence of ammonium citrate, etc.

Curtman and Frankel[6] suggest a qualitative method where they "have devised a scheme of analysis, by which small amounts of alkaline earth metals may be detected. The method consists in the precipitation of the alkaline earth metals together with a part of the lead as sulfates, with dilute sulfuric acid and alcohol from a solution of definite acidity. After extracting the lead sulfate with ammonium acetate, the alkaline earth sulfates are converted to carbonates by boiling with sodium carbonate solution. The carbonates are then dissolved in acetic acid and the resulting solutions analyzed in the usual manner."

In the face of such conflicting statements, on the one hand by Curtman and Frankel that good results are obtained by their method, and on the other hand the statements indicating that calcium and barium sulfates are somewhat soluble in ammonium salts, it was thought that it would be

[1] Storer, "Dictionary of Solubilities of Chem. Substances," Cambridge, 1864.

[2] THIS JOURNAL, **27**, 756 (1905).

[3] *Am. Chem. J.*, **22**, 217 (1899).

[4] *J. Phys. Chem.*, **9**, 210 (1905).

[5] Smithsonian Collection, *Misc.*, **21**, 81 (1879).

[6] THIS JOURNAL, **34**, 1493 (1912).

profitable to determine the solubilities of these substances in ammonium acetate solutions.

The ammonium acetate solutions for this work were prepared much as Noyes and Whitcomb have suggested. A standard HCl solution was made by precipitating and weighing silver chloride in the usual manner and a sodium hydroxide solution was standardized by titration with this acid. The ammonium hydroxide was standardized against the HCl with methyl orange as the indicator and the acetic acid (prepared by diluting the glacial acid) was standardized against the sodium hydroxide with phenolphthalein as the indicator. The titrations were all made by weight. The exact weights of ammonium hydroxide and acetic acid solutions were calculated and mixed carefully so as to get a "neutral" solution. A solution was prepared in this way which contained 21.37 g. of ammonium acetate per 100 g. of solution. The more dilute solutions were made by adding weighed portions of water.

The sulfates were purified material. In each case they were treated with water, filtered and washed repeatedly on a Büchner funnel to remove any soluble impurities. These operations were repeated twice. In the case of calcium sulfate a trace of carbonate was found which was destroyed with a little sulfuric acid in the first wash water.

In determining the solubilities, the solutions were saturated by shaking in a thermostat with a large excess of the solid sulfate for twelve to sixteen hours. In some cases the value was obtained by starting with either supersaturated or undersaturated solutions, while in other cases, when it had been proved that twelve hours was sufficient time for saturation, duplicate determinations were taken, one after twelve hours' shaking and the other after sixteen hours' shaking in the thermostat, starting with unsaturated solutions.

The sulfates in the saturated ammonium acetate solutions were determined directly by placing weighed portions of the solution in platinum dishes, evaporating to a few cc. on the water bath, adding a few drops of concentrated sulfuric acid and heating very cautiously until the ammonium sulfate thus formed and the excess of acid were removed, leaving the sulfate of the metal under test. Blanks were run on the method of determination and it was found that any one of the sulfates could be put through this process without any appreciable loss. The nonvolatile residue due to the solubilities of the glass of the bottles and the residue of the ammonium acetate was very little, less than 0.0005 g. in each case tried.

The specific gravities of the ammonium acetate solutions were determined at 25°, so that the solubility results given below can be calculated either by weight or by volume. The concentrations of the ammonium acetate in Table I and in the following tables are in terms of grams per 100 g. of ammonium acetate solution.

TABLE I.

Conc. of ammonium acetate	2.13	5.34	10.68	16.02	21.37
Sp. gr	1.005	1.012	1.024	1.036	1.045

These values are very nearly the same as those obtained by Hager[1] at 16°.

Table II gives the grams of lead sulfate soluble in 100 grams of ammonium acetate solutions at 25°. The first four values have been calculated from the data of Noyes and Whitcomb.[2]

TABLE II.

Conc. of ammonium acetate	0.000	0.796	1.591	3.170	5.34	10.68	21.37
Grams of lead sulfate	0.0041	0.0636	0.137	0.304	0.56	1.68	3.89

The solubilities of calcium sulfate in ammonium acetate solutions at 25° are given in Table III.

TABLE III.

Conc. of ammonium acetate	0.00	2.13	5.34	10.68	21.37
Grams of calcium sulfate	0.2085[3]	0.454	0.752	1.146	1.755

Table IV shows the solubilities of strontium sulfate in ammonium acetate solution of various strengths at 25°.

TABLE IV.

Conc. of ammonium acetate	0.00	2.13	5.34	10.68	21.37
Grams of strontium sulfate	0.0151[4]	0.0451	0.0732	0.0942	0.115

The solubilities of barium sulfate at 25° in water and in one concentration of ammonium acetate are given in Table V.

TABLE V.

Conc. of ammonium acetate	0.00	21.37
Grams of barium sulfate	0.00023[5]	0.016

When these values are plotted together on the same diagram, the curves indicate that at 25° the more concentrated the ammonium acetate solution the better will be the separation of the lead sulfate from the others. It is to be noted, however, that the solubilities, even of the barium and strontium sulfates, are considerable in ammonium acetate solution as compared to their solubilities in water. Also, it might be pointed out that no definite separation for the calcium sulfate could be made with ammonium acetate solution at ordinary temperatures.

In the qualitative method of separation of the sulfate suggested by Curtman and Frankel, "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." To get an idea of the solubilities of the sulfates in hot ammonium acetate solutions, each of the sulfates was di-

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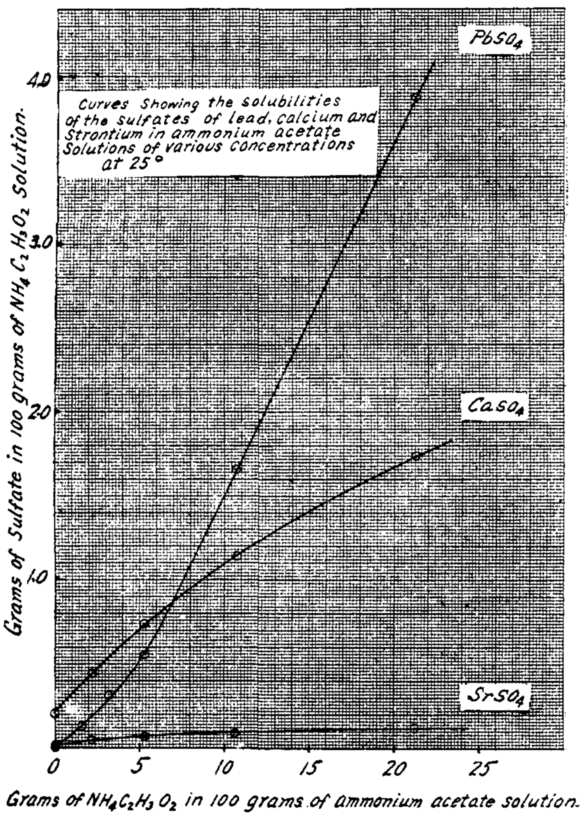
[1] "Manule Pharmaceuticum adjumenta varia," Leipsig, 1876.

[2] THIS JOURNAL, 24, 667 (1902).

[3] Hulett and Allen, THIS JOURNAL, 24, 667 (1902).

[4] Wolfman, *Osterr.-ung. Z. Zuckerind.*, 25, 988 (1896).

[5] Hulett, *Z. physik. Chem.*, 37, 398 (1901).



gested very gently at 100° in a 3 N solution of ammonium acetate for just ten minutes, a portion of the clear filtrate weighed out in a platinum dish evaporated nearly to dryness, cooled and the residue treated with a little sulfuric acid, ignited and weighed. Table VI shows the weights of the sulfates dissolved in this way in 100 grams of 3 N ammonium acetate solution. These tests are, to be sure, rough, but they will partially duplicate the conditions described above and will give an idea of the amounts which dissolve under these conditions.

Table VI.

Substance.	Weight of sulfate.
Barium sulfate	0.025
Strontium sulfate	0.142
Calcium sulfate	2.60
Lead sulfate	6.15

At first sight it would seem impossible to get very delicate results in testing for strontium if much ammonium acetate solution is used in washing the sulfates. A little experience indicated, however, that if the ammonium acetate solution contained a small amount of some soluble sulfate the solubilities of the barium and strontium sulfates were reduced. In 100 g. of 3 N ammonium acetate solution to which 1% of ammonium sulfate had been added the following amounts of sulfates were dissolved when treated in the same way as above at 100°.

Table VII.

Substance.	Weight of sulfate.
Barium sulfate	0.004
Strontium sulfate	0.010
Calcium sulfate	2.31
Lead sulfate	5.75

The addition of 1% of ammonium sulfate to the ammonium acetate solution diminishes the solubilities of barium and strontium sulfates enough for a qualitative separation, while larger amounts of calcium and lead sulfates are still soluble. We can, knowing this, explain why Curtman and Frankel obtained such good results in testing their method of analysis. They obtained conclusive tests for as little as 1 to 2 mg. of barium and strontium but admitted that in one or two cases where only 1 mg. of strontium was present the tests were faint. Curtman and Frankel made very few tests on small amounts of barium and strontium in absence of other sulfates the presence of which would lessen the solubility of the former. When several trials were made by their method, digesting the sulfates for ten minutes in 20 cc. of 3 *N* solution of ammonium acetate at 100° and washing the residue on the filter paper with a few cc. of the same hot solution, it took nearly 20 mg. of strontium to give a good test, if the other sulfates were not present. If a fairly large amount of the other sulfates like those of lead and calcium were present accurate results, such as the Curtman and Frankel table shows, could be obtained. The solubilities of the sulfates, when only washed on a filter paper with boiling hot ammonium acetate solution, were found to be smaller than when they were digested in the solution at 100° for ten minutes, but the values of the solubilities of the calcium and lead bore the same ratio to those of barium and strontium as before.

If a 3 *N* ammonium acetate solution containing 1% of ammonium sulfate was used for the solvent instead ot ammonium acetate alone, conclusive tests were obtained for as little as 3–5 mg. of strontium, calcium or lead and 1 to 2 mg. of barium, regardless of whether the other sulfates were present or not.

A modification of Curtman and Frankel's method is being used by Prof. J. A. Gibson[1] of this laboratory in his course in qualitative analysis. He uses the method immediately following the precipitation of the HCl group. He found, when alcohol was used to aid the precipitation of the sulfates, that occasionally a yellow precipitate appeared. This, according to Treadwell,[2] is a basic mercuric sulfate which is easily dissolved upon the addition of a small amount of dilute HCl.

A modification of Gibson's method is given below by the use of which a student should be able to identify with certainty a few milligrams of barium, strontium, lead and calcium. The calcium, if there is only a small amount present in the original solution, will be detected by ammonium oxalate either after removing the lead from the material soluble in ammonium acetate or after the ammonium sulfide separation.

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[1] "A System of Qualitative Analysis," Univ. of Mo., 1914.

[2] Treadwell and Hall, "Analytical Chemistry," Vol. 1, 148 (1911), John Wiley and Sons, New York.

Procedure.

If the volume of the solution is large, boil down to about 20 cc., add 3 cc. of 2 *N* sulfuric acid and an equal volume of ethyl alcohol. Let stand five minutes and filter. Wash twice with (1–1) alcohol-water mixture.

Wash the precipitated sulfates five times with a boiling 3 *N* ammonium acetate solution containing 1% of ammonium sulfate, using a wash bottle and allowing 5 cc. of ammonium acetate solution for each washing. Catch the filtrate in a porcelain dish.

Evaporate the ammonium acetate filtrate over a water bath to a sirupy consistency, cool, add concentrated sulfuric acid drop by drop (about 1 cc.) and dry the residue on the water bath. Heat the dish gently at first and then to a dull red later over the free flame to remove the ammonium sulfate and the sulfuric acid. Cool, put 5 to 10 cc. of normal sodium hydroxide solution in the dish and rub the residue with a stirring rod to loosen it. Filter the sodium hydroxide solution and make the filtrate acid with acetic acid. Add a few drops of potassium chromate solution; a yellow precipitate indicates the presence of lead.

The barium and strontium sulfates are converted to the carbonates by boiling in 4 *N* sodium carbonate solution and tested in the usual manner.

If a yellow precipitate comes down when the sulfuric acid and alcohol are added, add dilute HCl drop by drop with shaking till the yellow precipitate disappears. Accuracy cannot be attained if too much HCl is used in precipitation of the silver group.

In testing this method very good results were obtained, either when the sulfates were alone in the solution or when other groups were present.

A number of quantitative methods have been suggested for the separation of lead sulfate from the other sulfates by dissolving it in ammonium acetate solution. Leach,[1] for example, has suggested the determination of small amounts of lead in soft drinks by sulfating the ash and dissolving out the lead sulfate with ammonium acetate solution. The lead is subsequently determined colorimetrically with hydrogen sulfide. With this method probably there would be difficulty if copper or tin sulfates were in the sulfated ash, for these substances would go with the lead into the ammonium acetate solution.

No matter which method is used, if lead is to be determined by separating the sulfate from other substances by means of ammonium acetate solution, the ammonium acetate must first be removed before the lead thus obtained can be precipitated with accuracy.

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[1] "Food Inspection and Analysis," 1906, p. 704, John Wiley and Sons, New York.