color of chromyl chloride immediately vanishes and a brown precipitate is formed. The end point of the reaction is conveniently determined by the permanency of the red color of chromyl chloride upon the addition of an excess of that reagent. The brown precipitate, after being filtered, washed with carbon tetrachloride, and dried in a vacuum desiccator, was found to be an intimate mixture of silver chloride and a brown, lustrous powder, presumably chromyl acetate. An analysis of this mixture for the content of silver chloride and of chromic anhydride, the latter being calculated as chromyl acetate, gave the following results which substantiate the formation of chromyl acetate:

	Per cent.
Silver chloride	68.79
Chromyl acetate	31.08
Total	99.87

Chromyl acetate is a deliquescent substance and is readily hydrolyzed by water, yielding chromic and acetic acids. A suitable solvent for effecting its complete separation from silver chloride has not yet been found.

A further investigation of the properties of chromyl bromide and of chromyl acetate, and an extension of the reactions herein noted to the preparation of other chromyl compounds, is in progress.

THE PREPARATION OF AMMONIUM SELENATE: A NEW METHOD.[1]

By Frank C. Mathers and Roy S. Bonsib.

Received March 1, 1911.

Introductory Statement.

The object of this research was to determin the best conditions for the preparation of ammonium selenate by the treatment of either barium selenate or lead selenate with an excess of ammonium carbonate. This reaction forms insoluble barium carbonate or lead carbonate, with the ammonium selenate and the excess of ammonium carbonate in solution. This mixture is filtered and the filtrate is evaporated. During the heating, the excess of ammonium carbonate volatilizes and any barium or lead selenate which is in solution is precipitated. This precipitate is filtered off and the pure ammonium selenate allowed to crystallize.

The only method described[2] for the preparation of ammonium selenate is the saturation of selenic acid with ammonia. This method is undesirable because pure selenic acid, itself, is difficult to prepare.

In a method[3] similar to the one described in this paper, barium selenate

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[1] From a thesis to be submitted to the Faculty of Indiana University, for the degree of Master of Arts, by Roy S. Bonsib, 1911.

[2] Gmelin-Kraut, *Handbuch*, 1, 785 (1907).

[3] Gerichten, *Ann.*, 168, 214.

is treated with a slight excess of a solution of potassium carbonate. The filtrate from this mixture contains potassium selenate and the excess of potassium carbonate. The disadvantage of this process is that there is no good way of eliminating the excess of potassium carbonate. Potassium selenate cannot be used for the preparation of other selenates by double decomposition. Ammonium selenate is an excellent starting material for making the other selenates by double decomposition.

Barium and lead selenates were selected as starting materials on account of the ease with which they may be obtained in a pure condition. Pure selenic acid, which is difficult to make, is not required for the preparation of pure barium or lead selenate. Selenic acid containing the by-products of its formation may be used. Barium selenate and lead selenate are almost insoluble so they may be obtained by precipitation of any solution containing the SeO_4 ion with barium or lead nitrate. The barium or lead selenate thus formed may be purified easily by washing with water.

Experimental Manipulation.

Extraction of Metallic Selenium.—The selenium was extracted by the potassium cyanide method[1] from flue dust from the roasting of anode slimes from copper refining.

Preparation of Selenic Acid.—A nitric acid solution of selenium dioxide was oxidized to selenic acid with an excess of potassium permanganate. The precipitate of manganese dioxide was removed by filtration. The excess of potassium permanganate in the filtrate, as shown by the pink color, was decomposed with hydrogen peroxide.

Preparation of Barium Selenate.—Barium nitrate solution was added to the hot solution of selenic acid, prepared as described above. The precipitate of barium selenate was filtered and washed. For additional purification, this barium selenate was changed to barium carbonate and ammonium selenate by digestion with ammonium carbonate. The ammonium selenate solution, after separation from the barium carbonate by filtration, was evaporated to crystallization. Pure barium selenate was prepared by precipitating a solution of these crystals with barium nitrate.

Preparation of Lead Selenate.—Lead selenate was prepared in a manner similar to the method for making barium selenate. Lead selenate is more easily filtered and washed than the barium selenate.

Ammonium Carbonate.—Merck's "Ammonium Carbonate" was used. Its composition was: NH_3, 21.8, 21.4; CO_2, 27.7, 27.9 per cent.

Procedure.—Gram portions of barium or lead selenate were weighed out into small beakers and treated with varying quantities of distilled water and pulverized ammonium carbonate. After varying periods of

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[1] Nilson, *Ber.*, 7, 1719.

time, the mixtures were filtered and the residues washed with distilled water, until free from ammonium carbonate, and then analyzed to determin the yield.

Method of Calculating Yields.—The following is the equation for the reaction that takes place, M being either barium or lead:

$$MSeO_4 + (NH_4)_2CO_3 = MCO_3 + (NH_4)_2SeO_4.$$

The residue of either barium or lead carbonate, after filtering and washing free from the ammonium selenate and the excess of ammonium carbonate, was titrated with standard hydrochloric acid and sodium hydroxide. The barium or lead carbonate determined in this way was a measure of the ammonium selenate that was produced. The standard method for the determination of selenium, *i. e.*, precipitating the metallic selenium with sulfur dioxide, filtering, drying and weighing, was used in a few of the experiments as a check to show that the new method of calculating the yields was introducing no error. The titration method gave higher results in all cases, the difference being about 0.5 per cent.

Experimental Data.

Results with Barium Selenate.—Assuming the reaction

$$BaSeO_4 + (NH_4)_2CO_3 = BaCO_3 + (NH_4)_2SeO_4,$$

one gram of barim selenate is equivalent to 0.34 gram of ammonium carbonate. The analysis of the ammonium carbonate that was used in this work showed that it contained only 60 per cent. as much carbon dioxide as is contained in a compound of the composition $(NH_4)_2CO_3$. This analysis was not made until near the close of the work, which accounts for the fractional molecular parts of ammonium carbonate used in the tables.

In the following tables, 0.7 gram of ammonium carbonate represents 1.24 molecules of carbon dioxide to one molecule of barium selenate; 1.48 grams of ammonium carbonate represent 2.48 molecules of carbon

Ammonium carbonate. Grams.	Barium selenate. Grams.	Time treated. Hours.	Water used. cc.	Yield of ammon. selenate. Per cent.
0.7	1	15	5	46.87
0.7	1	29	5	53.38
0.7	1	35	5	55.99
1.4	1	18	10	75.52
1.4	1	24	10	87.23
1.4	1	39	10	91.14
2.8	1	4	10	40.36
2.8	1	8	10	62.50
2.8	1	12	10	74.21
2.8	1	24	10	87.23
2.8	1	28	10	96.35
2.8	1	36	10	97.65
2.8	**1**	**61**	**10**	**97.65**

dioxide to one molecule of barium selenate; and 2.8 grams of ammonium carbonate represent 4.96 molecules of carbon dioxide to one molecule of barium selenate.

This table shows that a large excess of ammonium carbonate is required. An almost theoretical yield is obtained with five equivalents of ammonium carbonate to one of barium selenate. Ammonium carbonate in excess of 2.8 grams will not dissolve in the amount of water used. The above table also shows that the reaction takes place very slowly, about thirty hours being required to obtain an approximately theoretical yield.

In the following table, one gram portions of barium selenate were treated with 2.8 gram portions of ammonium carbonate.

Time. Hours.	Water used. cc.	Yield of ammon selenate. Per cent.
17	15	72.91
17	20	63.80
17	25	57.29
17	30	49.48
28	15	83.33
28	20	82.03
28	25	72.91
28	30	60.01

This table shows that concentrated solutions give better yields.

Results with Lead Selenate.—Assuming the reaction

$$PbSeO_4 + (NH_4)_2CO_3 = PbCO_3 + (NH_4)_2SeO_4,$$

one gram of lead selenate is equivalent to 0.274 gram of ammonium carbonate. In the following tables, 0.274 gram of the ammonium carbonate that was used in this work represents 0.6 molecule of carbon dioxide to one molecule of lead selenate; 0.55 gram of ammonium carbonate represents 1.2 molecules of carbon dioxide to one molecule of lead selenate; and 1.1 grams of ammonium carbonate represent 2.4 molecules of carbon dioxide to one molecule of lead selenate, one gram of lead selenate being used in each case.

The following table shows that it is necessary to use 1.2 molecules of ammonium carbonate to one molecule of lead selenate, and that the reaction takes place comparatively rapidly. The change of dilution from five cc. to ten cc. is apparently of no effect as long as there is an excess of ammonium carbonate.

Experiments that are not given here show that stirring with air or continuous shaking is of no advantage.

The yields of ammonium selenate were almost theoretical. It is impossible to obtain a yield of 100 per cent. because a small amount of the lead carbonate dissolves[1] in the ammonium carbonate solution and in the wash water. When the solution of ammonium selenate and the wash

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[1] Olsen, "Quantitative Chemical Analysis," p. 123 (1905).

Ammon. carb. Grams.	Water used. cc.	Time. Hours.	Yield of ammon selenate. Per cent.
0.274	10	0.5	47.2
0.274	10	1	48.7
0.274	10	2	50.4
0.274	10	4	53.7
0.274	10	6	55.3
0.274	10	18	56.8
0.274	10	12	56.8
0.274	10	24	58.6
0.55	5	0.5	94.3
0.55	5	1	94.3
0.55	5	3	98.4
0.55	5	16	97.6
0.55	5	22	99.2
0.55	5	28	97.6
0.55	5	30	97.6
1.1	10	0.5	96.0
1.1	10	1	96.0
1.1	10	4	96.0
1.1	10	0.25	96.0
1.1	5	1	93.5
1.1	5	2	96.0
1.1	5	6	96.0
1.1	5	24	96.0

water from the lead carbonate residue are evaporated to drive off the excess of ammonium carbonate and to crystallize the ammonium selenate, the lead selenate is precipitated. This is, of course, filtered out to prevent contamination of the ammonium selenate. In one experiment the weight of this lead selenate was found to be 0.0172 gram; adding this to the yield of ammonium selenate obtained, gives a total of 99.47 per cent., which accounts for practically all of the lead selenate.

Summary.

The best conditions for the preparation of ammonium selenate by the treatment of barium selenate with ammonium carbonate were found to be:

1. 2.8 grams of ammonium carbonate (27.8 per cent. CO_2) to one gram of barium selenate, which is about five molecules of actual ammonium carbonate to one molecule of barium selenate.
2. 10 cc. of water to each gram of barium selenate.
3. The mixture should stand about thirty hours, with occasional shaking.

The best conditions, when using lead selenate with ammonium carbonate, were found to be:

1. 0.55 gram of the ammonium carbonate to one gram of lead selenate which is about 1.2 molecules of actual ammonium carbonate to one molecule of lead selenate.
2. Five cc. of water to each gram of lead selenate.

3. The mixture should stand about one or two hours to give the best yields, although good yields may be obtained in fifteen to thirty minutes.

The results of these experiments show that lead selenate is the better material to use because it gives a better yield and requires less ammonium carbonate and less time than does the barium selenate.

Increase of temperature, stirring with a current of air or carbon dioxide, or carrying out the reaction in sealed tubes does not increase the yield.

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A MODIFICATION OF THE DIPHENYLAMINE TEST FOR NITROUS AND NITRIC ACIDS.

BY W. A. WITHERS AND B. J. RAY

Received February 28, 1911.

Diphenylamine was discovered by Hofmann[1] in 1864, and the blue coloration which he found that it gives with various oxidizing agents has since been used for the detection of the presence of minute amounts of nitric acid.

In 1872 Kopp[2] first proposed its use for the detection of nitrous acid in commercial sulfuric acid.

In 1875 Böttger[3] proposed that the reaction of Kopp be used for the detection of the presence of nitrites and nitrates in potable waters.

Since that time various chemists have given consideration to the subject and have proposed modifications of the methods of applying the test—some of them being very delicate and others less so. It was the need of a reliable and delicate test for nitrites and nitrates which led us to take up this work.

For preparing the reagent Cohn[4] and Wiley[5] use diphenylamine and concentrated sulfuric acid and specify no relation between the amounts except that Wiley refers to 4 cc. of sulfuric acid. Fresenius[6] and Eggermainz[7] use 10 mg. and Muller[8] 20 mg. of diphenylamine to 100 cc. of concentrated sulfuric acid. Warrington[9] dissolves in an indefinit amount of water and adds an indefinit amount of concentrated sulfuric acid. Lunge[10] and Treadwell[11] use 500 mg. of diphenylamine for each 100 cc. of concentrated sulfuric acid and add 20 cc. of water. Hager[12] uses 1 gram to each 150 cc. of acid, and adds 30 cc. of alcohol, and Cimmino[13] uses 5 per cent. of hydrochloric acid without giving the relation between the diphenylamine and sulfuric acid.

The manner of making the test differs with different chemists. To 1 cc. of the liquid to be tested, the amount of diphenylamine reagent to be used is specified as "1 drop," "3 to 4 drops," "a few drops" and "5 cc.," and in some instances no amounts are stated. Some use also sul-