of all the results obtained with salt made from the amine is 58.995, and the average of the results with salt made from the crystallized chloride is 58.998. The very slight difference between these values lies within the experimental error of the determinations. Evidently, the salt was in all cases essentially free both from ammonium chloride and water. The almost complete absence of ammonium chloride was also shown by two experiments in which the amine was heated in a current of hydrochloric acid in the usual manner, and then the salt was dissolved in water and the cobalt was precipitated by the addition of ammonia-free sodium hydroxide. In one case where 1.76 grams of cobaltous chloride were used, the filtered solution, when tested with Nessler's reagent, showed the presence of 0.00025 gram of ammonium chloride, while in the other 2.13 grams of cobaltous chloride yielded 0.00005 gram of ammonium chloride. This proportion of impurity would have lowered the observed atomic weight 0.004 in the first case, and only 0.001 in the second. The average 0.003 is exactly the difference between the averages from the two samples of material. If this correction is applied in the analyses where the cobaltamine was used, the averages of both Series I and Series II are raised to 58.998, a negligible change.

Whether or not such a correction is applied the average of Series I and II confirms very closely the value 58.995 previously found by analysis of the bromide, hence the atomic weight of cobalt may, as before, be assumed to be 59.00 referred to silver 107.930.

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SEPARATION AND ESTIMATION OF BERYLLIUM.

BY CHARLES L. PARSONS AND S. K. BARNES.

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THE separation of beryllium from other elements presents little difficulty except in the case of aluminum and iron. It will invariably be found with aluminum in the last instance, and the problem therefore becomes the determination of beryllium in such a mixture.

Many methods for the separation of beryllium from iron and aluminum have been proposed but the one most often used has been founded upon the solubility of its hydroxide in ammonium carbonate which unfortunately dissolves also some of the hydroxides of aluminum and iron. Vauquelin[1] in 1798 first used ammonium carbonate, but his first separation depended upon the solubility of beryllium hydroxide in potassium hydroxide and its precipitation on boiling. Gmelin[2] and Schaffgotsch[3] both used this same method but it is very far from being accurate. Scheerer[4] first proposed the separation of the last traces of iron from the ammonium carbonate solution by means of ammonium sulphide. Berthier[5] suggested the use of ammonium sulphite as a reagent but the method was shown to be valueless by Böttinger.[6] In 1850 Rivot[7] proposed the ignition of the oxides in a current of hydrogen whereby the iron was reduced to metal and could be dissolved out with dilute nitric acid or its mass determined by the loss of weight. Debray[8] developed a separation dependent upon the action of zinc on the mixed sulphates precipitating the aluminum as a basic sulphate, but the method was never made quantitative. Joy[9] made a comparative study of all methods proposed to his time. Gibbs,[10] in 1864 for the first time, suggests the use of sodium fluoride to quantitatively separate aluminum from beryllium, and Pollok[11] shows that the fluoride separation is exceedingly sharp. Cooke,[12] after reducing the iron in hydrogen, volatilizes it in a current of hydrochloric acid. Havens and Way[13] accomplish the same result without previous reduction of the oxide. Rössler[14] succeeded in separating beryllium from small amounts of aluminum by precipitating with ammonium

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[1] Ann. chim. phys. 26, 155.

[2] Ann. Physik. 50, 175.

[3] Ibid. 50, 183.

[4] Ibid. 56, 479.

[5] Ann. chim. phys. [3] 7, 74.

[6] Ann. 51, 397.

[7] Ann. chim. phys. [3] 30, 188.

[8] Ibid. [3] 44, 1.

[9] Am. J. Sci. [2] 36, 83.

[10] Ibid. [2] 37, 346.

[11] Trans. Roy. Dublin Soc. [2] 1904, 139.

[12] Am. J. Sci. [2] 42, 78.

[13] Ibid. [4] 8, 217.

[14] Z. anal. Chem. 17, 148.

phosphate in the presence of citric acid. Vincent[1] uses dimethylamine to precipitate beryllium salts and finds that the aluminum compound is soluble in excess of the reagent. Iron acts like beryllium. Renz[2] confirms this, states the same to be true of methyl-, ethyl- and diethylamine, and claims the results to be quantitatively accurate. Zimmermann[3] in 1887 returns to the old potassium hydroxide and sulphite or thiosulphate method without any special addition. Scheier[4] in 1892, Atkinson and Smith[5] in 1895 and Burgass[6] in 1896 separate iron quantitatively from beryllium by means of nitroso-β-naphthol. Lebeau[7] precipitates the iron in nitric acid solution by ferrocyanide, removes the ferrocyanide by copper nitrate and the excess of copper by hydrogen sulphide. Hart[8] removes the major part of both iron and aluminum by careful precipitation of the sulphates with sodium carbonate, the beryllium being the last to precipitate, owing to the great solubility of its own hydroxide in its own sulphate. Havens[9] separates beryllium from aluminum quantitatively by the insolubility of hydrous aluminum chloride in a mixture of hydrochloric acid and ether which has been saturated with hydrochloric acid gas. Haber and Van Oordt[10] dissolve basic beryllium acetate in chloroform, leaving aluminum and iron acetates behind. Myers[11] removes iron electrolytically from a slightly acid solution of the sulphates, using a mercury cathode. Parsons and Robinson[12] separate beryllium basic acetate in a pure state from other acetates by means of its ready solubility in hot glacial acetic acid and comparative insolubility in the same reagent when cold.

PRELIMINARY INVESTIGATIONS.

Some qualitative work done by one of us some months ago had developed the fact that beryllium hydroxide was readily, im-

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[1] Bull. soc. chim. 33, 157.

[2] Ber. 36, 2751.

[3] Z. anorg. Chem. 15, 285.

[4] Chem. Ztg. 16, 420.

[5] This Journal, 17, 688.

[6] Z. angew. Chem. 1896, 596.

[7] Compt. rend. 121, 641.

[8] This Journal, 17, 604.

[9] Am. J. Sci. [4] 4, 111.

[10] Z. anorg. Chem. 40, 465.

[11] This Journal, 26, 1124.

[12] Ibid. 28, 555.

mediately and apparently completely separated from aluminum and ferric hydroxides by boiling momentarily in a saturated solution of acid sodium carbonate. No trace of aluminum could be found in the separated beryllium compound by Haven's method[1] and the white hydroxide of beryllium or its hydrochloric acid solution showed scarcely a trace of color. The object of this investigation was to determine whether or not this reaction could be made strictly quantitative.

Solutions of pure aluminum chloride and pure beryllium chloride were made and analyzed, and it was early apparent on attempting to get closely agreeing results by precipitating the beryllium as hydroxide with ammonia that some source of error existed. After some experimenting it was found that the beryllium hydroxide, when freed of the ammonium chloride present, passed into the colloidal condition on washing with pure water and indeed much more rapidly than is known to be the case with aluminum. On adding a small amount of ammonium acetate to the wash-water the difficulty immediately disappeared and no trouble was experienced in obtaining well-agreeing results even in fairly strongly ammoniacal solution. Small amounts of beryllium hydroxide also adhere tenaciously to the glass of the precipitating beaker and after as perfect mechanical removal as possible the beaker should be treated with a little dilute nitric acid and the contained beryllium reprecipitated. Beryllium oxide obtained by blasting the hydroxide is somewhat hygroscopic and should be weighed with due precautions.

SEPARATION AND DETERMINATION.

The method is based on the total insolubility of aluminum and ferric hydroxide in a 10 per cent. boiling acid sodium carbonate solution and on the total solubility of beryllium hydroxide in the same. From the aluminum solution used the aluminum hydroxide was totally precipitated by the boiling hot saturated solution of acid sodium carbonate and the beryllium solution gave a perfectly clear solution with the same. The acid sodium carbonate employed was in the form of small crystals and contained but a trace of the normal carbonate as indicated by phenolphthalein.

Portions of the solutions of beryllium and aluminum chlorides were weighed out containing amounts convenient to work with,

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[1] Loc. cit.

and washed from the weighing-bottle into clean Jena beakers of 250 cc. capacity in which the separation was made.

The solution was made up to about 100 cc., neutralized as nearly as possible with ammonia and 10 grams of solid acid sodium carbonate added. If the solid carbonate is added to any but a cold solution spattering will take place.

The beakers were kept covered with watch-glasses to prevent loss of material by any escaping gas during the heating and the solution was brought to a boil as quickly as possible and allowed to boil not to exceed one minute. Carbon dioxide is not evolved very rapidly till the boiling temperature is nearly reached if the solutions are neutral, but evolution of gas must not be mistaken for boiling.

The solution was now set in cold water and cooled, filtered and washed two or three times with hot water. The precipitate was dissolved on the filter with as little as possible (1:1) hydrochloric acid and run back into the same beaker in which the precipitation was first made, the solution made up to 100 cc., made neutral with ammonia, precipitated again with acid sodium carbonate as before, cooled, filtered and washed with hot water, running both filtrates together. A cloudiness will be noticed in the combined filtrates after washing, which looks as if aluminum hydroxide were coming through but this is not the case, the cloudiness being due to the dilution of the strong acid sodium carbonate solution with water. The aluminum hydroxide was again dissolved in (1:1) hydrochloric acid, precipitated with ammonia and determined in the ordinary way, as it was found that it was next to impossible to wash out all the acid sodium carbonate from the gelatinous precipitate.

The filtrate from the double precipitation, containing the beryllium in solution, was carefully acidified with strong hydrochloric acid in a covered beaker as special care was required that the escaping gas should not cause mechanical loss. Just before neutralization a portion of the beryllium was thrown down as hydroxide but this immediately dissolved on addition of more acid. The solution was then boiled to remove carbon dioxide so that no ammonium carbonate should be formed, precipitated with ammonia, boiled, allowed to settle and filtered, washing with ammonium acetate solution until free from chlorides. The beryllium hydroxide was ignited to constant weight, which is readily attained, and weighed.

Results follow:

Al_2O_3		BeO.		Total.	
Taken	Found.	Taken.	Found.	Taken.	Found.
0.1252	0.1266	0.0818	0.0810	0.2070	0.2076
0.1323	0.1336	0.0795	0.0781	0.2118	0.2117
0.0942	0.0957	0.0573	0.0563	0.1515	0.1520
0.0869	0.0881	0.0610	0.0588	0.1479	0.1469
0.0907	0.0945	0.0629	0.0594	0.1536	0.1539

The results are slightly too high in aluminum oxide and correspondingly low in beryllium oxide although the totals found agree closely with the theoretical amounts. The aluminum hydroxide showed therefore, as was to be expected, a tendency to occlude some beryllium hydroxide. Washing the first and second precipitation with hot acid sodium carbonate solution was next tried and this seemed to assist in removing the beryllium, although small amounts were still left behind in the aluminum hydroxide as the following results will show.

Al_2O_3.		BeO.		Total.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0.0840	0.0849	0.0646	0.0642	0.1486	0.1491
0.0740	0.0749	0.0680	0.0676	0.1420	0.1425
0.2059	0.2055	0.0972	0.0977	0.3031	0.3032
0.6152	0.6167	0.0372	0.0348	0.6524	0.6515
0.1327	0.1346	0.3125	0.3107	0.4452	0.4453
0.1368	0.1386	0.3050	0.3031	0.4418	0.4417
0.6233	0.6250	0.0730	0.0714	0.6963	0.6964

Trials were made of heating the acid sodium carbonate solution in pressure flasks so that no carbon dioxide might escape, but the results were not satisfactory.

By the procedure so far followed the mixed hydroxides were first precipitated together in the cold and the beryllium hydroxide dissolved in the boiling reagent. This would seemingly tend to allow the aluminum hydroxide to so enclose some of the solid beryllium hydroxide that the reagent could not act upon it. This was particularly the case when relatively large amounts of aluminum were present. To overcome this difficulty as much as possible, separations were tried by adding the boiling hot mixture of the chlorides to a nearly boiling solution of acid sodium carbonate containing enough of the reagent to make the mixed liquid an approximately 10 per cent. solution. The whole was then brought to a boil, held there for half a minute, cooled and treated as before. By this procedure only the aluminum was precipitated as hydroxide and less beryllium was mechanically retained. Larger amounts of aluminum were used in this case than before and as the results could be interpreted from the beryllium alone the aluminum was not weighed.

BeO.	
Taken.	Found.
0.1311	0.1307
0.1424	0.1415
0.2522	0.2515
0.0671	0.0664
0.0642	0.0631

To show the application of this same procedure in the presence of iron, ferric chloride was added in variable amounts, both large and small, to mixtures of aluminum and beryllium chlorides, boiled with a little nitric acid to insure oxidation and the whole treated as above. The combined hydroxides of iron and aluminum were several times the mass of the beryllium hydroxide yet the separation was almost complete and the resulting beryllium oxide was analytically pure.

BeO.	
Taken.	Found.
0.2152	0.2146
0.0911	0.0906
0.0825	0.0806
0.1020	0.0995

Considering the well-known great tendency of gelatinous hydroxides like those of aluminum and iron to retain other substances which may be present, this separation of beryllium leaves little to be desired. Care must, of course, be exercised to bring the acid sodium carbonate quickly to a boil and to boil for a moment only, for if too much carbon dioxide is lost the aluminum may partially pass into solution.

CONCLUSIONS.

Beryllium hydroxide must be washed with water containing an electrolyte to prevent the loss of colloidal hydrate through the filter.

Beryllium can be quantitatively separated from iron and aluminum by means of the solubility of its hydroxide in a boiling hot solution of acid sodium carbonate of approximately 10 per cent. strength.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H., June 1, 1906.