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John H. McClure
Iowa State College

Charles V. Banks
Iowa State College

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An Empirical Titrimetric Method for the Determination of Beryllium *

By JOHN H. McCLURE AND CHARLES V. BANKS

INTRODUCTION

Recently, in connection with a study of the metallurgy of beryllium, a rapid and accurate method was needed for the determination of this metal. A review of the literature revealed that the existing titrimetric methods are based on hydrolysis, neutralization or precipitation reactions. These methods are outlined briefly below.

1. Direct titration of a beryllium salt with sodium hydroxide using phenolphthalein as the indicator (3).

2. An iodometric titration of the acid resulting from the hydrolysis of a beryllium salt (3, 10).

3. Hydrolysis of a fluoberyllate in the presence of calcium chloride followed by titration with sodium hydroxide using phenolphthalein as the indicator (4, 17).

4. Hydrolysis of a fluoberyllate in the presence of calcium chloride followed by an iodometric titration of the resulting acid (11).

5. Precipitation of beryllium hydroxide followed by dissolution in excess hydrochloric acid and the iodometric determination of the excess acid (7).

6. Precipitation of small amounts of beryllium by titration with a standard quinalizarin solution (8, 9).

7. Potentiometric titration of beryllium solutions with standard sodium fluoride solution (16).

8. Titration of beryllium solutions with sodium hydroxide, ammonium hydroxide or triammonium phosphate. The progress of the titration is followed by means of a high frequency titrimeter (13).

The first four of these methods are not easily adaptable to the analysis of metal samples and the next two are limited in that they are applicable only to small amounts of beryllium. Method seven does not appear to give sufficiently sharp breaks in the titration curve to give good results and method eight requires a somewhat intricate and expensive piece of equipment.

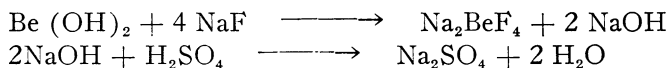
Since the existing titrimetric methods could not satisfactorily be

* Work performed in the Ames Laboratory, Atomic Energy Commission.

adapted to the routine analysis of beryllium metal, the following method was developed.

THEORETICAL

This method is based on the reaction of beryllium hydroxide with an alkali metal fluoride to give an alkali metal fluoberyllate and free alkali which can be titrated with an acid.



APPARATUS AND REAGENTS

Apparatus. The pH measurements were made with a Type E glass electrode using a Beckman Industrial Model pH meter.

Beryllium Acetylacetonate. Beryllium acetylacetonate was prepared and purified according to the method of Arch and Young (2). This material was used in the form of a nitric acid solution which was analysed by two different methods, that of Parsons (12) and that of Cupr (6).

The results obtained by the two methods are given in Table 1.

Table 1

Standardization of Beryllium Solution

Method	BeO found, mg./ml.
Parsons -----	5.12
	5.12
	5.13
Cupr -----	5.15
	5.13
Average-----	5.13

Beryllium Basic Acetate. Beryllium basic acetate was prepared and purified by distillation according to Archibald (1). Parsons (12) used this compound of beryllium for molecular weight determinations. This material was analysed by the method used by Parsons after which a weighed amount was made up in nitric acid and diluted to a known volume.

Nitric Acid. Reagent grade.

Sodium Fluoride. Reagent grade.

Potassium Fluoride. Reagent grade.

Sodium Hydroxide. A 2.5 *N* sodium hydroxide solution was prepared from reagent grade alkali.

Hydrochloric Acid. A 0.5 *N* hydrochloric acid solution was

prepared from reagent grade acid and standardized against standard alkali.

Solutions of Diverse Ions. Solutions of diverse ions were prepared from reagent grade salts of these metals.

EXPERIMENTAL WORK

Reference pH Values. The first problem was the determination of the pH to be used for a reference point from which to calculate the amount of beryllium in the sample. This was done by taking an aliquot of a standard solution of beryllium and titrating it to a pH 11.0 ± 0.2 with standard base and then back with standard acid. The results obtained are shown by curves 1 and 2, Fig. 1. From this figure it is evident that the pH which is most sensitive with regard to the amount of acid added is 8.5. Hence it appears that pH 8.5 would be a good point from which to begin measuring the acid used for the actual titration. Having fixed on this optimum pH value an aliquot containing 0.2600 gm. of beryllium oxide was taken and diluted to 1 liter with distilled water. This solution was adjusted to a pH of 11.1 by the addition of the 2.5 *N* sodium hydroxide. Dilute hydrochloric acid solution was then added to adjust the pH to 8.5. Five grams of sodium fluoride was added and the pH rose to 10.45. The resulting solution was then titrated with standard 0.5 *N* acid. The result obtained is shown by curve 3 in Fig. 1. The break which occurred when 38.96 ml. of 0.5134 *N* acid had been added is similar to the break obtained in titrating a strong base with a strong acid. The mid-point of this break which occurs at pH 7.5 was taken as the end-point of the titration. The volume of acid added to reach pH 7.5 after the addition of the sodium fluoride is used to calculate the amount of beryllium in the sample. In the above case 0.2511 gm. of beryllium oxide was recovered. This is less than the amount known to be present.

Effect of Sodium Fluoride. It was found that two different bottles of sodium fluoride gave different results. Both bottles used were produced by the same commercial source and bear the same maximum limit of impurities. Both samples were checked by the the method of Rosin (14) and passed the specifications laid down. The samples were analysed spectrographically but there was no detectable difference. Table 2 shows the results obtained using the two different lots of sodium fluoride. Also shown in Table 2 are the results obtained using two different samples of potassium fluoride. An appreciable difference in the two different samples of potassium fluoride used was also found. In order to eliminate the possibility than an anion, such as carbonate, was causing the trouble

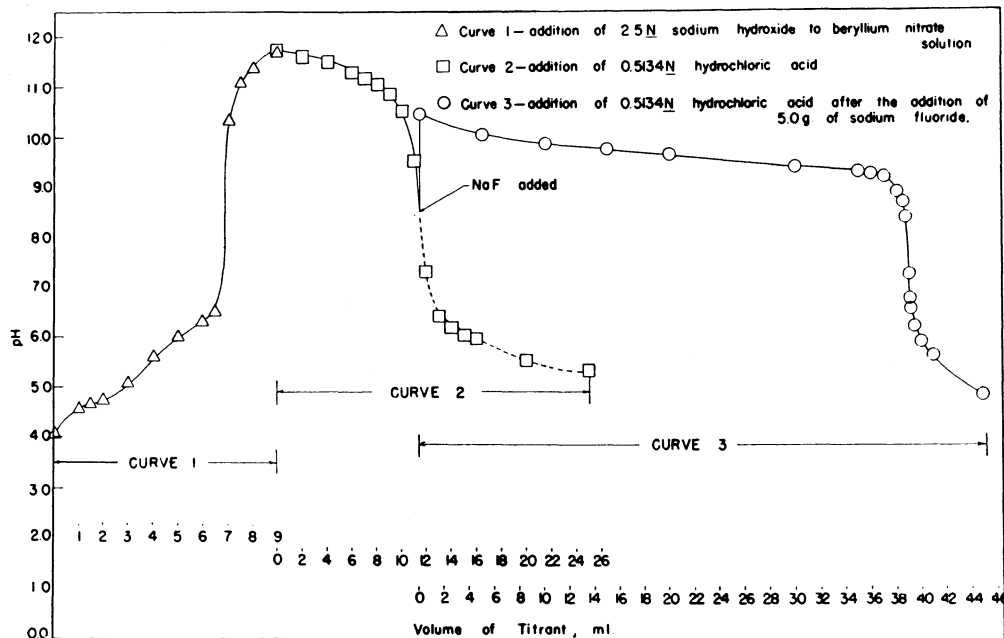


Figure 1— Selection of reference points for the titrimetric determination of beryllium

hydrochloric acid was added to a solution of sodium fluoride and the solution boiled. This solution was then cooled and the pH adjusted to 7.0 after which it was added to a beryllium solution. The resulting solution was then titrated in the usual manner. The same difference in the two lots of sodium fluoride found previously was observed. When the lot of sodium fluoride which gave the lower result was recrystallized according to the method of Tananaev (15) it was found possible to bring the results up to that obtained with the better lot. Table II also shows these results. Recrystallization of the better lot did not improve the results.

Table 2

Effect of Sodium Fluoride

BeO Taken, gm.	Vol. Acid, ml.	Normality Acid	BeO Found,* gm.	Error, mg.	Titer, gm. BeO/ml. x 10 ³	Fluoride Used
0.2496	37.83	0.5134	0.2427	-6.9	6.599	KF Lot 50
0.2492	37.90	0.5134	0.2432	-6.0	6.575	KF Lot C245
0.2051	30.99	0.5145	0.1994	-5.7	6.618	KF Lot C245
0.2051	30.99	0.5145	0.1994	-5.7	6.618	KF Lot C245
0.2050	31.07	0.5145	0.1998	-5.2	6.598	KF Lot C245
0.2051	30.99	0.5145	0.1994	-5.7	6.618	NaF Lot D004
0.2051	30.71	0.5145	0.1970	-8.1	6.679	NaF Lot 52
0.2510	34.20	0.5750	0.2458	-5.2	7.339	NaF Lot D004
0.2503	33.50	0.5750	0.2408	-9.5	7.472	NaF Lot 52
0.2486	33.94	0.5750	0.2439	-4.7	7.325	NaF Lot 52
						recryst.
0.2491	37.10	0.5156	0.2391	-10.0	6.714	NaF Lot D004 neutralized
0.2495	36.60	0.5156	0.2358	-13.7	6.817	NaF Lot 52 neutralized

* BeO found based on the normality of the acid used.

From these data it may be seen that it is necessary to standardize the procedure using a given bottle of fluoride, which standardization may or may not change when a new bottle of fluoride is used.

Effect of Excess Fluoride. The data of Table 3 show that from 130% to 790% excess of fluoride has no effect on the precision of the method.

Table 3

Effect of Excess Fluoride

BeO Taken, gm.	Vol. HCl, ml.	BeO Found, gm.	Gms. Fluoride Added	Error, mg.	% Excess fluoride	Titer, gm. BeO/ml. x 10 ³
0.2050	30.99	0.1994	2.5 gm. KF	-5.6	131%	6.615
0.2050	31.01	0.1995	7.5 gm. KF	-5.5	395%	6.611
0.2050	31.01	0.1995	15 gm. KF	-5.5	790%	6.611

Effect of Sodium Carbonate. It was observed that the carbonate ion had an effect on the results obtained. Table 4 will illustrate the anomalous effect observed. Sodium carbonate added after the solution had been made basic, lead to higher results although still not stoichiometric, while sodium carbonate added when the solution was acid gave low results. The effect of removing all the carbonate from the sodium hydroxide with barium chloride is also shown. The latter effect is rather small as the sodium hydroxide used was very low in carbonate originally.

Table 4
Effect of Sodium Carbonate

BeO Taken, gm.	Vol. of 0.5145 N HCl, ml.	BeO Found, gm.	Error, mg.	Titer gm. BeO/ml. x 10 ³	Miscellaneous
0.2050	31.07	0.1998	-5.2	6.598	No Carbonate Added.
0.2050	31.14	0.2003	-4.7	6.583	Carbonate removed from NaOH with BaCl ₂ .
0.2050	31.19	0.2005	-4.5	6.573	0.3 gm. Na ₂ CO ₃ added while solution was alkaline.
0.2050	30.89	0.1987	-6.3	6.636	0.3 gm. Na ₂ CO ₃ added while solution was acid.

Effect of Diverse Ions. For the purpose of examining interfering ions a titer of gm. BeO/ml. was determined for a given acid. After the titer was determined samples of beryllium were taken and various cations were added in known amounts and the beryllium determined in the usual manner. Calculations were made using the titer instead of the normality of the acid, the results obtained are shown in Table 5.

Table 5
Interference of Various Cations

BeO Taken, gm.	Diverse Ion, Kind	ppm Present* x 10 ⁻³	BeO Found, gm.	Error, mg.
0.2099	Al ⁺ ₃	7	0.2113	+1.4
0.2099	Bi ⁺ ₃	13	0.2102	+0.3
0.2099	Ca ⁺ ₂	6	0.2102	+0.3
0.2099	Fe ⁺ ₂	13	0.2102	+0.3
0.2099	Pb ⁺ ₂	13	0.2099	±0.0
0.2099	Mg ⁺ ₂	16	0.2095	-0.4
0.2099	Mn ⁺ ₂	10	0.2104	+0.5

* Parts of diverse ion per million parts beryllium.

The error caused by the aluminum can be corrected for if the percentage of aluminum present is known. By a consideration of the difference in valence and molecular weight between beryllium and aluminum it can be shown that any given percentage of beryllium will be high by one-half the percentage of aluminum present. This calculation was checked by adding some aluminum and carrying out a determination. The results agreed very well.

Effect of Sample Size. The effect of varying the sample size was studied and the results are recorded in Table 6. For the purpose of comparison all quantities have been reduced to a common basis by calculating a titer. From the table it may be seen that sample size appears to have no effect on the precision of the method, at least over the range investigated.

Precision of the Method. Table 7 shows that the method has a precision of better than two parts per thousand (ppt).

DISCUSSION

It is evident from the results given above that, (1) the chemical reactions taking place are not accurately represented by the equations given earlier, or (2) there is some impurity in the reagents

Table 6

Effect of Sample Size

BeO Taken, gm.	Vol. of 0.5145 N HCl, ml.	BeO Found, gm.	Titer, gm. BeO/ml. $\times 10^3$
0.1282	19.43	0.1249	6.598
0.2050	31.01	0.1995	6.611
0.2564	38.74	0.2492	6.618
0.3076	46.49	0.2992	6.616
0.3847	57.98	0.3729	6.635

Table 7

Precision of the Method*

BeO Taken, gm.	Vol. of 0.5174 N HCl, ml.	BeO Found, gm.	Error, mg.	Titer, gm. BeO/ml. $\times 10^3$	Error,** ppt
0.2050	30.89	0.1998	-5.2	6.636	+1.4
0.2100	31.70	0.2050	-5.0	6.625	-0.3
0.2049	30.94	0.2001	-4.8	6.622	-0.8
0.2049	30.94	0.2001	-4.8	6.622	-0.8
0.2153	32.47	0.2100	-5.3	6.631	+0.6
0.1999	30.17	0.1951	-4.8	6.626	-0.2

* KF Lot C245 used.

** Calculated as deviation from the mean titer of 6.627.

used which is interfering. Considerable time was spent on trying to devise some other mechanism which would correctly represent the reactions taking place but to no avail. The fluoride was checked from several angles in the hope of making the results stoichiometric but this was not accomplished. These attempts have already been mentioned and the results obtained given.

The method is precise to about two parts per thousand, when using any given bottle of fluoride and any given caustic.

The recovery is quantitative when a titer is used, for samples below about 0.35 gm. BeO.

Large excesses of fluoride have no effect on the precision of the method.

Carbonate ion interferes. The interference leads to higher or lower results depending on whether the carbonate is added while the solution is alkaline or acid. The results are still not stoichiometric.

RECOMMENDED PROCEDURE

Weigh out a sample of beryllium metal of such size that a convenient aliquot of its solution will contain 0.1 to 0.3 g. of beryllium oxide and cautiously dissolve in dilute sulfuric acid. After the sample is completely dissolved the solution is evaporated to strong fumes of sulfur trioxide to eliminate any fluoride that might be present. Where fluoride is known to be absent nitric acid may be used. The resulting solution of beryllium sulfate or nitrate is diluted to a known volume and suitable aliquots are taken for analysis. These aliquots are diluted to about 1000 ml. and 2.5 *N* sodium hydroxide added until the pH is 11.0 ± 0.2 . These solutions are allowed to stand for two or three minutes, the pH is adjusted to 8.5 by the addition of dilute hydrochloric acid which has been standardized against a solution of known beryllium content. The beryllium titer of the hydrochloric acid should be about 0.006 g. beryllia per ml. Seven grams of potassium fluoride or its equivalent in sodium fluoride is added to each aliquot and the pH readjusted to 7.5. This latter volume is used to calculate the percentage beryllium in the solution. A type E glass electrode should be used for the pH adjustments since indicators give very indefinite end points under the conditions of the above titration.

APPLICATIONS

This method is applicable to the analysis of beryllium metal, beryllium oxide, and soluble beryllium salts.

SUMMARY

The Craig method (5) for titrating aluminum has been modified and applied to the determination of beryllium. This method consists of adjusting the pH of a solution of beryllium to 8.5 followed by the addition of sodium or potassium fluoride and titration of the liberated sodium hydroxide with a standard acid solution. A precision of better than two parts per thousand is obtained. A glass electrode is used for the pH adjustments.

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