Analytical Chemistry of Beryllium. VI. 8-Hydroxyquinaldine as a Reagent for Determination of Beryllium

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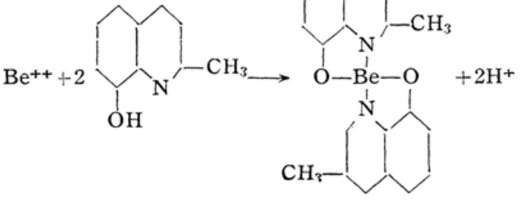
Introduction

8-Hydroxyquinaldine, one of the derivatives of 8-hydroxyquinoline, "oxine", was found to be used as a favourable analytical reagent for the determination of beryllium. There has been reported no adaptable organic reagent to determine beryllium, and it has been desired to discover such a preferable reagent as oxine in the determination of aluminum, so the author firmly believes that the analytical method of beryllium based upon the use of this new reagent, is the most valuable. It was found possible to determine, both gravimetrically and volumetrically, 2 to 10 milligrams of beryllium. The methods to be described are simple, rapid, and accurate.

In general, 8-hydroxyquinaldine is very similar to oxine in its analytical properties, except that it does not precipitate aluminum neither in acetic acid-acetate nor in ammoniacal solutions¹⁾. As regards beryllium, although it has been reported that 8-hydroxyquinaldine forms no quantitative precipitate in ammoniacal solutions²⁾, it gives well-defined yellow crystalline precipitate, which fluoresces strongly under ultraviolet light with a green color, as shown in Fig. 1, and this precipitate dried when either in a desiccator over sulfuric acid at room temperature, or in a drying oven at 110°C, corresponds to the formula $Be(C_{10}H_8NO)_2$.

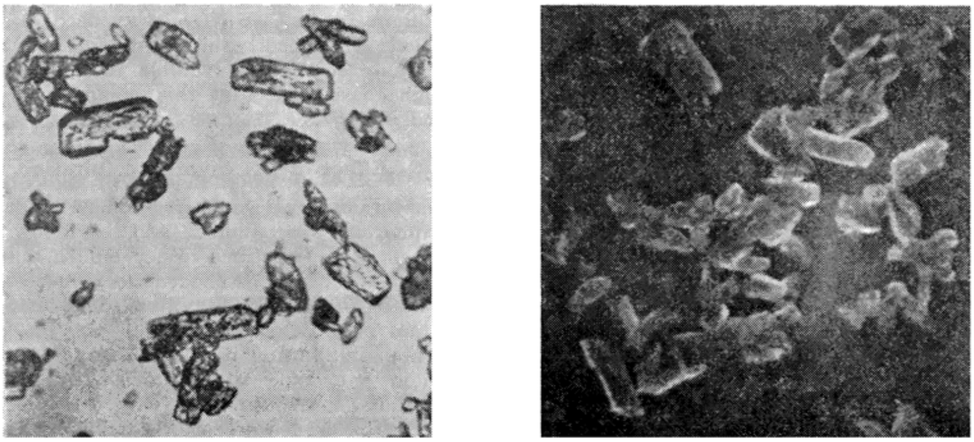
The following equation, with the beryllium compound represented as a possible chelate, best describes the reaction involved.



In the development of a volumetric method for the beryllium, use is made of the fact that the reagent can be quantitatively brominated in hydrochloric acid medium, such as oxine²⁾.

Reagents

Preparation of 8-Hydroxyquinaldine.—Crude 8-hydroxyquinaldine was prepared by a method similar to that described by Phillips and his coworkers²⁾, and the purification was made by the following procedure.



A B

Fig. 1. Microphotograph of beryllium precipitate of 8-hydroxyquinaldine (×260).
A: In ordinary light. B: In ultra-violet light.

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1) L. L. Merritt, J. K. Walker, *Ind. Eng. Chem., Anal. Ed.*, **16**, 387 (1944).

2) J. P. Phillips, J. E. Emery, J. P. Price, *Anal. Chem.*, **24**, 1033 (1952).

Dissolve 20 g. of crude 8-hydroxyquinaldine in 40 ml. of glacial acetic acid by warming, dilute to 1 l. with water, and remove the insoluble materials by filtering. Heat gently this filtrate to 70°C, and add 70 ml. of 1 M cupric sulfate solution and 150 ml. of 2 N ammonium acetate solution. Allow to stand for half an hour on water bath to digest the precipitate of 8-hydroxyquinaldine complex of copper. Collect the precipitate, wash several times with hot water and then dissolve in the smallest possible quantity of hot hydrochloric acid. Then dilute to 500 ml. with water, heat to boiling, pass hydrogen sulfide into the solution to precipitate copper as sulfide, and filter. Boil the filtrate gently to remove the dissolving hydrogen sulfide, cool, nearly neutralize with concentrated sodium hydroxide solution and make slightly alkaline with sodium bicarbonate. By steam distillation of the resulting mixture, pure 8-hydroxyquinaldine comes over. More purified product for use in this investigation is obtained by recrystallization from 60% ethyl alcohol, of which melting point is 73° to 73.5°C.

The recovery of this reagent can be made by the above procedure.

8-Hydroxyquinaldine Solution.—In 4 ml. of glacial acetic acid 2 g. of the reagent was dissolved by heating, and diluted to 100 ml. with distilled water. This solution is stable for a week or longer.

Standard Beryllium Solution.—About 14 g. of beryllium basic acetate, purified by vacuum sublimation[3], was treated with 40 ml. of sulfuric acid (1:1), heated gently to remove most of acetic acid, and then the volume was brought to 250 ml. Estimation of beryllium contained in this solution was made by the ordinary beryllium oxide method. Working solution was prepared by exactly diluting 100 ml. of this solution to 1 l. with distilled water.

Standard Potassium Bromate-Bromide Solution, 0.1 N.—Exactly 2.784 g. of C. P. potassium bromate and 10 g. of C. P. potassium bromide were dissolved in distilled water and diluted to 1 l.

Standard Sodium Thiosulfate Solution, 0.1 N.—About 25 g. of reagent grade sodium thiosulfate were dissolved in 1 l. of distilled water. The standardization of this solution was made by using the above 0.1 N potassium bromate-bromide solution.

Other Reagents.—The other reagents were prepared from reagent or C. P. grade chemicals.

Properties of Beryllium Precipitate of 8-Hydroxyquinaldine

Thermal Stability.—The precipitate of beryllium 8-hydroxyquinaldine complex could be dried to constant weight in an hour at 110°C, and by further heating at this temperature for several hours, no decrease of the weight was found. Even when it was heated at 150°C for an hour, the decrease of the weight was less than 1 per cent.

Composition.—The fact that the composition of this precipitate has a formula $Be(C_{10}H_8NO)_2$, was certified by the following estimations of both amounts of beryllium and 8-hydroxyquinaldine which are present in the precipitate dried at 110°C. Beryllium was gravimetrically determined as BeO by igniting the precipitate in the platinum crucible. The results are shown in Table I.

TABLE I

AMOUNT OF BERYLLIUM IN THE PRECIPITATE

Sample	Precipitate taken.	BeO found,	Be in the precipitate	
	g.	g.	g.	%
A	0.5117	0.0384	0.0138	2.70
B	0.5555	0.0432	0.0156	2.80
C	0.5045	0.0381	0.0137	2.72
Theoretical value for $Be(C_{10}H_8NO)_2$				2.77

The amount of 8-hydroxyquinaldine was titrated, after dissolving the precipitate in hydrochloric acid, with standard solution of potassium bromate-bromide[2]. Table II gives the results.

TABLE II

AMOUNT OF 8-HYDROXYQUINALDINE IN THE PRECIPITATE

(1 ml. of 0.1 N $KBrO_3 \equiv 0.003980$ g. of 8-Hydroxyquinaldine)

Sample	Precipitate taken,	0.1 N $KBrO_3$ wanted,	8-Hydroxyquinaldine in the precipitate,	
	g.	ml.	g.	%
A	0.1912	46.76	0.1861	97.33
B	0.1867	45.54	0.1812	97.06
C	0.0922	22.78	0.0907	98, 37
Theoretical value for $Be(C_{10}H_8NO)_2$				97.85

As may readily be seen from Tables I and II, the results obtained in the analysis of the precipitate very closely correspond with the theoretical values. Further proof of the validity of this structural formula is found in the fact that 0.02770, the theoretical value of the gravimetric factor for beryllium in $Be(C_{10}H_8NO)_2$, was used in all calculations with good results. In addition, the fact that this precipitate is soluble in chloroform is enough to assume that this compound has no bound water[4].

Effect of pH upon Precipitation

The optimum pH range for complete beryllium precipitation was studied, and the following experiment was performed to accomplish this.

To 10 ml. of the standard beryllium solution, containing 5.10 mg. of beryllium, 5 ml. of 4 N ammonium chloride solution, 5 ml. of 10% sodium tartrate solution and various amounts of 4 N ammonium hydroxide were added. The solution was diluted to about 50 ml. with distilled water, heated to 60°C on water bath, and then 12 ml. of 8-hydroxyquinaldine solution was added drop by drop with stirring. The precipitate was digested for about half an hour, filtered through a sintered-

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[3] M. Ishibashi, K. Motojima, *J. Chem. Soc. of Japan*, (Pure Chem. Sec.), 72, 100 (1951).

[4] F. Feigl (Translated by P.E. Oesper), "Chemistry of Specific, Selective and Sensitive Reactions", (1949), p. 184.

glass filter crucible (porosity No. 4), washed with dilute ammonium hydroxide (1 : 100), dried at 110°C to constant weight, and weighed, while the pH of filtrate was determined by Beckman glass electrode pH meter Model H2. The per cent precipitate was plotted against pH as shown in Fig. 2.

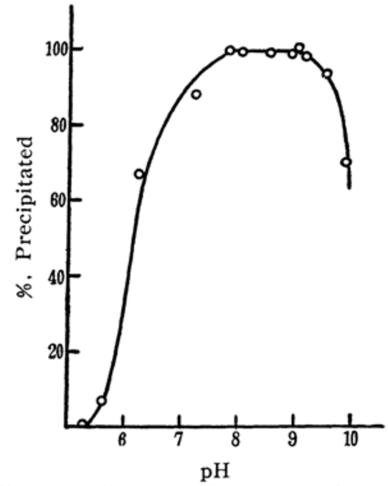

Fig. 2. Effect of pH on precipitation of beryllium 8-hydroxyquinaldine complex.

From the curve, shown in Fig. 2, it can be seen that the pH range of complete precipitation is between 7.8 and 9.2.

Gravimetric Determination

A number of beryllium determinations in which various amounts of beryllium were present, were made following gravimetric procedure.

Procedure.—To a solution containing from 2 to 10 mg. of beryllium, add 5 ml. of 4 N ammonium chloride solution and 5 ml. of 10% sodium tartrate, and then the volume is brought to about 50 ml. The solution is heated to from 60° to 70°C, and the pH is brought up to about 9 with 2 N ammonium hydroxide, thymol blue test paper being used. Then, sufficient amount of 8-hydroxyquinaldine solution is added, dropwise with stirring, so as to contain from 20 to 30 per cent in excess of the amount necessary to precipitate completely the beryllium present in solution. The resulting precipitate is digested at this temperature for about half an hour, to facilitate crystallization of the precipitate, and then, the precipitate is filtered through a weighed sintered-glass filter crucible (porosity No. 4), washed several times with small portions of dilute ammonium hydroxide (1 : 100), and dried at 110°C to constant weight, which will be obtained in about half an hour. The weight of beryllium present in the sample is calculated by multiplying the weight of precipitate by gravimetric factor 0.02770.

In the above procedure, a large amount of tartrate must not be added, because it prevents the coagulation of precipitate. On the other hand, beryllium precipitate can also be prepared without addition of sodium tartrate by following modification of procedure. To a warmed sample beryllium solution, containing ammonium chloride, firstly add 8-hydroxyquinaldine solution and then raise pH to 9 by the adding of dilute ammonium hydroxide, drop by drop with stirring. The precipitate is treated similarly as before.

Some of the results are shown in Table III.

TABLE III

GRAVIMETRIC DETERMINATION OF BERYLLIUM

Beryllium taken, mg.	Weight of precipitate, g.	Beryllium found, mg.	Error, mg.
2.55	0.0926	2.57	+0.02
2.55	0.0917	2.54	−0.01
5.10	0.1820	5.04	−0.06
5.10	0.1857	5.11	+0.01
5.10	0.1840	5.10	0.00
5.10	0.1828	5.06	−0.04
5.10	0.1825	5.06	−0.04
10.20	0.3634	10.07	−0.13
10.20	0.3723	10.31	+0.11
10.20	0.3725	10.32	+0.12

Volumetric Determination

Beryllium may be determined volumetrically, making use of the fact that 8-hydroxyquinaldine is readily and quantitatively brominated to form 5,7-dibromo-8-hydroxyquinaldine. The beryllium chelate of 8-hydroxyquinaldine is dissolved in hydrochloric acid, and treated with excess standard potassium bromate-bromide solution. The excess of bromate is determined iodometrically by back titration with standard thiosulfate. These reactions are based upon the following equations.

$$Be^{++}+2C_{10}H_8NOH \longrightarrow Be(C_{10}H_8NO)_2+2H^+ \quad (a)$$

$$Be(C_{10}H_8NO)_2+2HCl \longrightarrow Be^{++}+2C_{10}H_8NOH+2Cl^- \quad (b)$$

$$2C_{10}H_8NOH+4Br_2 \longrightarrow 2C_{10}H_6Br_2NOH+4HBr \quad (c)$$

From Equation (a) and (c), it is evident that one atom of beryllium is equivalent to 8 atoms of bromine, therefore 1 ml. of 0.1 N potassium bromate-bromide solution should correspond to 0.1127 mg. of beryllium.

Varying amounts of beryllium were determined volumetrically by the following procedure based upon above mentioned reactions.

Procedure.—The chelate, containing from 2 to 10 mg. of beryllium, after being precipitated and washed similarly as in the gravimetric procedure, is dissolved in hot 6 N hydrochloric acid, in which case 20 ml. or more is necessary in proportion to the amount of precipitate, and transferred to a glass-stoppered flask. To this solution add a few drops of 0.1% solution of methyl red as indicator, then titrate slowly with standard potassium bromate-bromide solution with constant stirring, and after the color has changed to yellow, add a few milliliters of standard potassium bromate-bromide solution. Stopper the flask, allow it to stand for a few minutes, add 1 g. of potassium iodide, and titrate 0.1 N sodium thiosulfate solution using starch as indicator. From the amount of standard potassium bromate-bromide solution required to brominate the 8-hydroxyquinaldine, the weight of beryllium may be calculated. As before, 1 ml. of 0.1 N potassium bromate-bromide solution corresponds to 0.1127 mg. of beryllium. Some of the results are represented in Table IV.

TABLE IV

VOLUMETRIC DETERMINATION OF BERYLLIUM

Beryllium taken, mg.	0.1 N $KBrO_3$-KBr used, ml.	Beryllium found, mg.	Error, mg.
5.10	45.55	5.13	+0.03
5.10	45.19	5.09	+0.01
5.10	46.92	5.29	+0.19
5.10	45.76	5.16	+0.06
5.10	45.10	5.09	−0.01
5.10	44.78	5.05	−0.05
5.10	45.55	5.13	+0.03
2.55	22.77	2.57	+0.02
2.55	22.60	2.54	−0.01

Effect of Diverse Ions

About 1 g. of alkali and ammonium salts of chloride, nitrate, sulfate and acetate do not interfer with the determination of beryllium. The metal ions which precipitate with 8-hydroxyquinaldine in ammoniacal solutions, such as bismuth, cadmium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, silver, titanium, and zinc do interfere with the procedure. When aluminum is present, though it gives no precipitation with this reagent, a large amount of tartrate must be added to prevent its hydroxide from coming down, and a relatively large amount of tartrate hinders the coagulation of beryllium chelate. So that, any excess amount of aluminum more than 0.5 mg. must be removed before the beryllium is determined.

The separating methods of beryllium from iron and aluminum were especially studied, and the following procedure, which is based upon the fact that iron and aluminum can be removed by the extraction of their oxinate in acetic acid-acetate solutions with chloroform, was found very useful. The sample solution, containing not more than 20 mg. of iron and aluminum and having a volume about 40 ml., is treated with sufficient amounts of 5% oxine acetic acid solution to precipitate iron and aluminum, and the pH is adjusted to from 4.5 to 5 with 2 N ammonium acetate solution. Then the oxinates of iron and aluminum and the excess of oxine are extracted with five 10 ml. portions of chloroform. After the resulting solution is heated gently to expel the droplets of chloroform, beryllium is determined. By this method, these metals which can not be separated from beryllium by mercury cathod electrolysis[5], such as titanium also can be removed. But in this case titanium must be less than 10 mg.

Conclusion

The methods for determining beryllium with 8-hydroxyquinaldine, described here are fairly sensitive and the procedures are simple. The precipitate formed is well-defined insoluble crystalline, easily filtered and washed, and thermally stable. The gravimetric factor is very small, 0.02770, and the volumetric factor is low, 1 ml. of 0.1 N potassium bromate solution corresponding to 0.1127 mg. of beryllium, so that, a few milligrams of beryllium can be determined, both gravimetrically and volumetrically, with good accuracy.

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[5] A. D. Melaven, *Ind. Eng. Chem., Anal. Ed.*, **2**, 180 (1930).