Analytical Chemistry of Beryllium. VII. Spectrophotometric Determination of Micro Quantities of Beryllium with 8-Hydroxyquinaldine

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Introduction

The colorimetric methods for the determination of micro quantities of beryllium which have been recently reported were based on the lake formation with such dyes as quinizarin-2-sulfonic acid¹⁾, aurintricarboxylic acid²⁾, alkannin³⁾ and naphthazarin³⁾. On the whole, these reactions are not specific and even small amounts of aluminum and iron interfere with the determination of beryllium. The method which has been investigated by the author and is described below, is fundamentally different from the above mentioned ones, and is more specific for beryllium.

In the previous paper⁴⁾ it was reported that beryllium forms slightly soluble chelate with 8-hydroxyquinaldine in ammoniacal medium, which has a formula $Be(C_{10}H_8NO)_2$, and that beryllium can be determined both gravimetrically and volumetrically with this reagent. The spectrophotometric method is based on the property that this chelate is soluble in chloroform and can be extracted by this solvent. The resulting chloroform

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1) M. W. Cucci, W. F. Neuman and B. J. Mulryan, *Anal. Chem.*, **21**, 1358 (1949).

2) G.E. Kosel and W.F. Neuman, ibid., **22**, 936 (1950).

3) A.L. Underwood and W.F. Neuman, ibid., **21**, 1348 (1949); T.Y. Toribara and A.L. Underwood, ibid., **21**, 1352 (1949).

4) K. Motojima, This Bulletin, "Analytical Chemistry of Beryllium", VI.

solution is colored light yellow, and beryllium is determined by photometry of this extract. The method for determination of beryllium is made by the following procedure: first from the chelate of 8-hydroxyquinaldine by adding acetic acid solution of this reagent to the beryllium solution and adjusting the pH to 8.0±0.2, next extract the chelate with chloroform, and then measure the absorbancy of this extract at the wave length of 380 mμ. The reason why this wave length is chosen is that beryllium chelate of 8-hydroxyquinaldine in chloroform absorbs most strongly at this wave length, while the reagent alone in this solvent absorbs strongly below 370 mμ.

Apparatus

A Beckman Model DU spectrophotometer with 1.00 cm. glass cell was used for all absorbancy measurements. A Beckman glass electrode pH meter Model H2 was used for the pH measurements.

Reagents

Standard Beryllium Solutions.—Several standard beryllium solutions were prepared in the same way as was shown in the previous work[4], each 10 ml. of these solution contained 5.3, 10.5 and 21.0 micrograms of beryllium.

8-Hydroxyquinaldine Solution.—Dissolve 2 g. of pure 8-hydroxyquinaldine prepared by the previously described method[4], in 4 ml. of glacial acetic acid by heating and dilute to 200 ml. with distilled water.

Chloroform. — Chloroform was purified by washing several times respectively, with 6 N sulfuric acid, aqueous solution 2 N in ammonium hydroxide and in ammonium chloride and then water, drying over anhydrous calcium chloride and then distilling. The recovery of chloroform was also made by this procedure.

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

Experimental

Absorption Spectra.—Absorption spectra of beryllium chelate of 8-hydroxyquinaldine in chloroform were studied. Approximately 50 ml. of solutions, containing 10.5 and 21.0 micrograms of beryllium, 5 ml. of 10 % ammonium chloride solution, 3 ml. of 8-hydroxyquinaldine solution and proper amount of dilute ammonium hydroxide to attain the pH to 8.0±0.2, were extracted with each 10.0 ml. of chloroform. The resulting chloroform solutions were dried with anhydrous sodium sulfate and absorbancies were measured over a wave length range of 360 to 470 mμ. The data obtained are given in Fig. 1. From these absorption spectra, it is seen that beryllium chelate of 8-hydroxyquinaldine in chloroform has an absorption maximum at 380 mμ. Accordingly, this wave length has been chosen for the determination of beryllium.

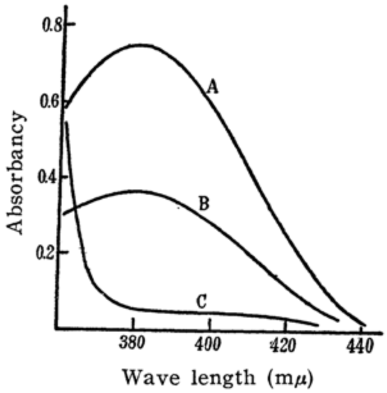


Fig. 1. Absorption spectra of beryllium chelate of 8-hydroxyquinaldine in chloroform.
A : 21.0 micrograms of Be.
B : 10.5 micrograms of Be.
C : blank.

Effect of pH on Extraction.—To determine the proper pH for the most efficient extraction of beryllium, the following series of experiments were made. Approximately 50 ml. of solutions containing 10.5 micrograms of beryllium, 3 ml. of 8-hydroxyquinaldine solution and sufficient amounts of either acetic acid and acetate or ammonium hydroxide and ammonium chloride to attain the desired pH, were extracted with each 10.0 ml. of chloroform. Measurements of pH were made on the aqueous layers after extraction. The extracts were dried with anhydrous sodium sulfate and then the absorbancies were determined at 380 mμ versus chloroform. The results obtained are shown in Fig. 2. Extraction is seen to be complete over a pH range 7.5 to 8.5. A similar experiment was made about the reagent, and it was found that the blanks were

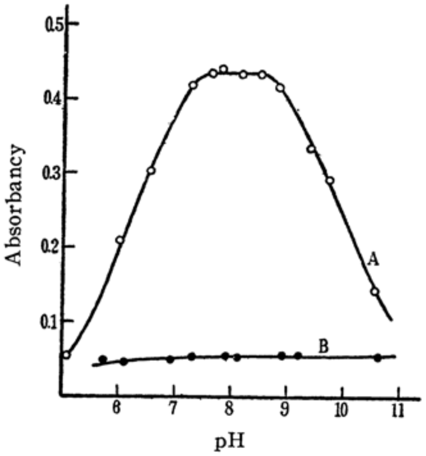
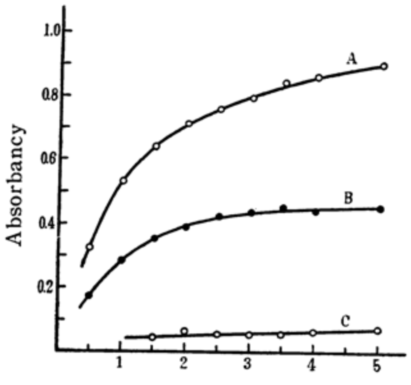


Fig. 2. Effect of pH on extraction of beryllium chelate of 8-hydroxyquinaldine.
A : 10.5 micrograms of Be.
B : blank.

reasonably constant in this pH range. So that the optimum pH range for the extraction is from 7.5 to 8.5.

Amount of Reagent.—Approximately 50 ml. of solutions containing 10.5 and 21.0 micrograms of beryllium respectively, and varying amounts of 8-hydroxyquinaldine solution, were extracted with each 10.0 ml. of chloroform at a pH 8.0±0.2. Then the measurements of the absorbancy at 380 mμ, versus chloroform, were made on these dried extracts. A similar set but with no beryllium present was also run. These results are shown in Fig. 3.

In case that more than 2.5 ml. of reagent solution is added, the rate of increase of these absorbancies is not very large, and as to the case when 10.5 micrograms of beryllium is present, the absorbancies after correction for the blank reading are almost constant. So that 3 ml. of 8-hydroxyquinaldine solution has been selected as a suitable amount of reagent.



Reagent added (ml.)

Fig. 3. Effect of reagent on absorbancy.
A: 21.0 micrograms of Be.
B: 10.5 micrograms of Be.
C: blank.

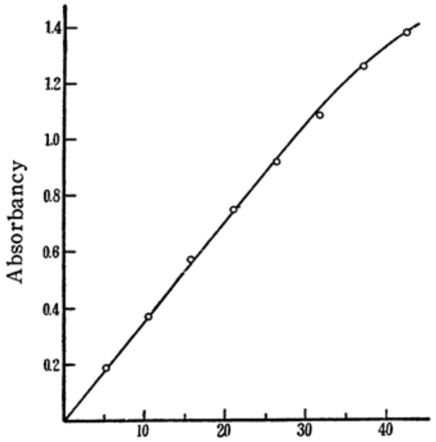
Effect of Digestion.—When extraction was made without digestion, the recovery of beryllium showed somewhat low values, but not so large an effect of digestion was observed, and it was confirmed that the digestion for from fifteen to thirty minutes at room temperature is most suitable.

Stability.—The absorbancy of the dried extract, stored in an amber glass bottle with a glass stopper, was found to remain unchanged for three days or more.

Spectrophotometric Procedure and Preparation of Calibration Curve

About 35 ml. of slightly acidic solution containing not more than 30 micrograms of beryllium, is treated with 5 ml. of 10% ammonium chloride solution and 3 ml. of 8-hydroxyquinaldine, solution, and the pH of the resulting solution is adjusted to 8.0±0.2 with 2N ammonium hydroxide. The solution is transferred to a cone-shaped 130 ml. separatory funnel which is graduated at 50 ml., with a few milliliters of rinsed water, and the volume is brought to 50 ml. After standing for half an hour, extraction is made with 10.0 ml. of chloroform added from automatic measuring pipette[5], by vigorous shaking for a minute. The chloroform layer is drawn off into a small amber glass bottle with glass stopper, containing a gram of anhydrous sodium sulfate, and is shaken to remove droplets of water. Then the absorbancy of this extract is measured at 380 mμ using blank as a reference. Beryllium is determined by the use of a calibration curve which is prepared by similar treatment of a series of a known amount of beryllium.

The calibration curve was prepared by taking 5.3, 10.5, 15.8, 21.0, 26.3, 31.5, 36.8, and 42.0 micrograms of beryllium. The result is shown in Fig. 4. As will be seen from this curve, a close approximation to a linear relationship between beryllium concentration and the absorbancy is obtained up to 30 micrograms.



Micrograms of Be

Fig. 4. Calibration curve of beryllium. (at the wave length of 380 mμ)

Interfering Substances

A few grams of sodium, potassium and ammonium salts of acetate, sulfate, chloride and nitrate do not interfere with this procedure. Less than 1 mg. of phosphate ion, 15 mg. of magnesium and 5 mg. of calcium also do not interfere with this procedure.

A small amount of aluminum, not more than 100 micrograms, does not interfere with this procedure, but when more than that exists it precipitates its hydroxide that prevents the extraction, therefore more than 100 micrograms of aluminum must not be present. Tartrate, though it is useful for the prevention of aluminum precipitation, must not be added, because it hinders the complete extraction of beryllium chelate. Bismuth, cadmium, chromium, copper, cobalt, indium, iron, nickel, tin, titanium and zinc ions do interfere with this procedure, because they form

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[5] K. Motojima, *J. Chem. Soc. of Japan* (*Pure Chem. Sec.*), **76**, 903 (1955).

chelates of 8-hydroxybuinaldine or hydroxide, but these metals, except titanium, can be simply and rapidly removed from beryllium by mercury-cathode electrolysis⁶⁾, and such metals as copper, cadmium, iron, nickel and zinc may be masked by use of cyanide.

The separating method of beryllium from relatively large amounts of aluminum, iron and titanium, and determination method of beryllium in the presence of a minute amount of iron were especially studied.

Determination of Beryllium in Presence of Iron

Ferric iron yields a dark bluish chloroform solution under the same condition and interferes seriously with the determination of beryllium, but its absorption spectrum is entirely different from that of beryllium, and has two absorption maxima at the wave length of 470 and 580 mμ, as is shown in Fig. 5. Beer's law is obeyed at 580 and 380 mμ, respectively, as is shown in Fig. 6, while beryllium chelate has no absorption at 580 mμ. Therefore, beryllium can be determined in presence of a small amount of iron, not more than 50 micrograms, by making a correction for the amount of iron present.

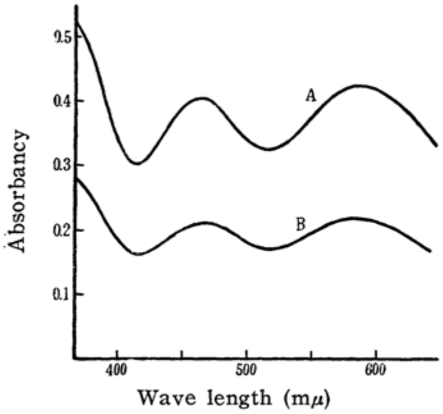

Fig. 5. Absorption spectra of ferric chelate of 8-hydroxyquinaldine in chloroform.
A : 50.0 micrograms of Fe.
B : 25.0 micrograms of Fe.

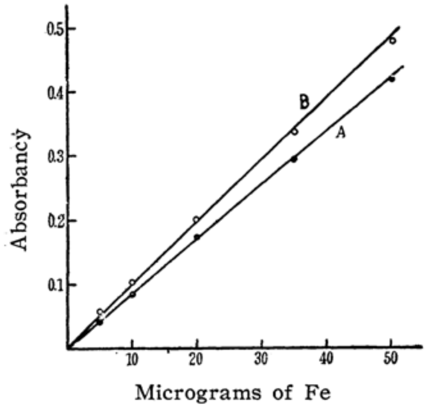

Fig. 6. Calibration curves of iron.
A : at 580 mμ.
B : at 380 mμ.

The following formula holds⁷⁾ :

$$C_{\mathrm{Be}}=\frac{a_{580}^{\mathrm{Fe}}A_{380}-a_{380}^{\mathrm{Fe}}A_{580}}{a_{380}^{\mathrm{Be}}\cdot a_{580}^{\mathrm{Fe}}}$$

where, C_{Be} : beryllium present, A : absorbancies measured, a : absorbancy index (the absorbancy per microgram of beryllium or iron).

The values of a_{380}^{Be}, a_{380}^{Fe} and a_{580}^{Fe} are found from the calibration curves for beryllium and iron at 380 and 580 mμ, respectively. In this experiment these values are as follow:

$$a_{380}^{\mathrm{Fe}}=0.0098, \quad a_{580}^{\mathrm{Fe}}=0.0085,$$
$$a_{380}^{\mathrm{Be}}=0.0352.$$

A number of mixed solutions containing known amounts of beryllium and iron in various ratios were prepared and beryllium was determined by making the above correction. Some of these results are shown in Table I, which seem to be quite satisfactory.

TABLE I
DETERMINATION OF BERYLLIUM IN PRESENCE OF IRON

Be Taken, Microgram	Fe Added, Microgram	Absorbancy, Measured		Be Found, Microgram	Error, Microgram
		380 mμ	580 mμ		
5.3	10.0	0.283	0.085	5.1	−0.2
5.3	25.0	0.441	0.207	5.7	+0.4
10.5	10.0	0.470	0.088	10.5	0.0
10.5	25.0	0.622	0.212	10.7	+0.2
21.0	10.0	0.860	0.089	21.6	+0.6
21.0	25.0	0.990	0.216	21.1	+0.1
31.5	10.0	1.170	0.087	30.4	−1.1
31.5	25.0	1.330	0.209	30.9	−0.6

Extraction Separation Method with Oxine

Such metals as aluminum, copper, iron, nickel and titanium which precipitate chloroform-soluble oxinate from acetic acid and acetate medium can be quantitatively separated from beryllium by the following procedure. Of these metals, aluminum, iron and titanium were especially studied.

About 40 ml. of slightly acidic solution containing not more than 20 mg. of aluminum, 20 mg. of iron and 10 mg. of titanium, and a suitable amount of beryllium, is treated with a sufficient amount of 5 % oxine acetic acid solution to make oxinate of these metals, and the pH of the solution is adjusted to from 4.5 to 5.0 with 2N ammonium acetate solution. Then the oxinate of these metals and the excess of oxine are extracted with five 10 ml. portions of chloroform. The resulting solution is heated gently to expel the droplets of chloroform, and the volume is brought to about 40 ml. by evaporation. After cooling, beryllium is

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

7) E.B. Sandell, "Colorimetric Determination of Traces of Metals". New York, (1950), p. 70.

determined with the above mentioned procedure. In this case it is desirable to measure the absorbancy at 580 $\mathrm{m}\mu$ and, if necessary, make a correction for iron which seems to be accidentally mixed in the solution during the procedure. Some of the results are shown in Table II, which seem to be satisfactory.

TABLE II

THE RESULTS OF EXTRACTION SEPARATION METHOD WITH OXINE

Be Taken, Microgram	Metals Added Milligram,			Absorbancy Measured,		Be Found, Microgram	Error, Microgram
	Fe	Al	Ti	380 $\mathrm{m}\mu$	580 $\mathrm{m}\mu$		
10.5	—	—	—	0.383	0.011	10.5	0.0
21.0	—	—	—	0.735	0.003	20.8	−0.2
0.0	20	—	—	0.016	0.010	0.1	+0.1
10.5	20	—	—	0.375	0.004	10.5	0.0
21.0	20	—	—	0.732	0.003	20.7	−0.3
0.0	—	20	—	0.012	0.002	0.4	+0.4
10.5	—	20	—	0.382	0.002	10.8	+0.3
21.0	—	20	—	0.740	0.011	20.7	−0.3
0.0	—	—	10	0.021	0.000	0.6	+0.6
10.5	—	—	10	0.361	0.001	10.2	−0.3
21.0	—	—	10	0.763	0.011	21.3	+0.3
10.5	5	5	2	0.373	0.015	10.1	−0.4
21.0	10	10	2	0.744	0.025	20.3	−0.7

Conclusion

The spectrophotometric method for determination of microquantities of beryllium with 8-hydroxyquinaldine was established. By this method from 2 to 30 micrograms of beryllium in about 40 ml. can be determined simply and accurately. Small quantities of aluminum do not interfere with this method, and even in the presence of a minute amount of iron, beryllium can be determined by making a correction for the amount of iron persent. Therefore complete separation of aluminum and iron is not necessary. Moreover, the separation method of beryllium from relatively large amounts of iron, aluminum and titanium was studied.

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