Analytical Chemistry of Beryllium. VIII. Fluorometric Determination of Micro Quantities of Beryllium with 8-Hydroxyquinaldine

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Introduction

In the previous paper[1] it was reported that the beryllium chelate of 8-hydroxyquinaldine could be quantitatively extracted with chloroform and that the extract was successfully used for the spectrophotometric determination of micro quantities of beryllium. As this chloroform extract containing beryllium chelate of 8-hydroxyquinaldine shows strong yellowish green fluorescence under ultraviolet light, the following investigation was undertaken to see whether or not this fluorescence was reproducible enough for a fluorometric method for beryllium.

Beryllium chelate of 8-hydroxyquinaldine was extracted with chloroform by a way similar to that mentioned in the previous work[1], then the fluorescence of the extract was measured, and it was found possible to determine from 0.3 to 3 micrograms of beryllium in about 40 ml. of solution without

1) K. Motojima, This Bulletin, "Analytical Chemistry of Beryllium. VII."

difficulty. Therefore the sensitivity of this method is nearly equal to that of the morine method developed by Sandell[2], but is better than that of the quinizarin method established by Fletcher and others[3].

Apparatus

A fluorometric attachment for Beckman Model DU spectrophotometer with a tungsten lamp as the light source, was used for fluorescence measurement. A primary filter transmits a band of wave-lengths centering at 360 mμ, and a secondary filter which is transparent to all wave-lengths longer than about 430 mμ, were used. The reason why this secondary filter was selected, was that the wave-length band of the fluorescent light produced by the beryllium chelate of 8-hydroxyquinaldine in chloroform was approximately distributed from 450 to 625 mμ, which was observed by the visual method using a spectrometer.

All the other apparatuses were the same as were used in the previous work[1].

Reagents

Standard Beryllium Solution.—Several standard beryllium solutions were prepared by exactly diluting the standard solution used in the previous work[1]. Each 10 ml. of these solutions contained 0.53, 1.05 and 2.10 micrograms of beryllium.

Standard Quinine Sulfate Solution.—Quinine sulfate (0.100 g., reagent grade) was dissolved and diluted to 1 l. with 0.1N sulfuric acid. This solution was exactly diluted with 0.1N sulfuric acid to yield a solution containing 1 microgram of quinine sulfate per milliliter.

Other Reagents. — 8-Hydroxyquinaldine solution, chloroform and the other reagents were prepared in the same way as was mentioned in the previous work[1].

Procedure and Preparation of Calibration Curve

Approximately 35 ml. of slightly acidic solution containing from 0.3 to 3 micrograms of beryllium, is treated with 5 ml. of 10% ammonium chloride solution and 2ml. of 8-hydroxyquinaldine solution, and the pH of the solution is adjusted to 8.0±0.2 with 2N ammonium hydroxide. The solution is transferred to a separatory funnel with a few milliliters of rinsed water, and the volume is brought to 50 ml. By the same procedure mentioned in spectrophotometric method[1], extraction is made with 10.0 ml. of chloroform, and the chloroform solution is dried with unhydrous sodium sulfate. Then the fluorescence of this chloroform solution is measured with a Beckman photofluorometer setting the chloroform at 0 and the standard quinine sulfate solution to 100 (or 50 when the fluorescence of the sample solution is stronger than this standard) on the transmittancy scale with the selector switch in the 1 position. Beryllium is determined by the use of the calibration curve prepared by similarly treating a series of known amount of beryllium.

The calibration curve was prepared by taking from 0.26 to 7.35 micrograms of beryllium. The result is shown in Fig. 1. As will be seen from this curve, an approximation to a linear relationship between beryllium concentration and the intensity of fluorescence is obtained up to 3 micrograms.

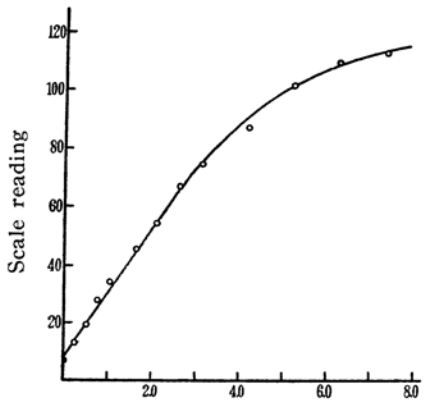

Fig. 1. Calibration curve for fluorometric determination of beryllium.

Effect of Variables

Effect of pH.—A series of several solutions each containing 2.10 micrograms of beryllium in about 35 ml. was treated with 2 ml. of 8-hydroxyquinaldine solution and suitable amounts of acetic acid and ammonium acetate or ammonium hydroxide and ammonium chloride to fall within a pH range of from 4 to 10. Then the extraction was made and the fluorescence of the extract was measured, respectively, by the above mentioned procedure. The results are shown in Fig. 2, and the approximately constant fluorescence is obtained in the pH range from 7.5 to 8.3.

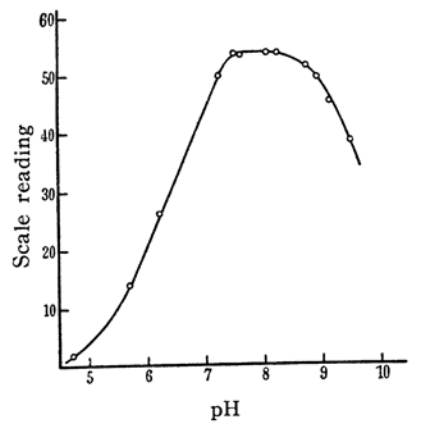

Fig. 2. Effect of pH on fluorometric determination of beryllium.

2) E.B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 674, 762 (1940); E.B. Sandell, *Anal. Chim. Acta*, **3**, 89 (1949).
3) M.H. Fletcher, C.E. White and M.S. Sheftel, *Ind. Eng. Chem., Anal. Ed.*, **18**, 179 (1946).

Ammount of Reagent.—Approximately 50 ml. of solutions each containing 2.10 micrograms of beryllium, 5 ml. of 10% ammonium chloride solution, varying amounts of 8-hydroxyquinaldine solution, and a suitable amount of dilute ammonium hydroxide, enough to adjust the pH to 8.0±0.2, were extracted with 10.0 ml. of chloroform respectively. Then, the fluorescences of these dried extracts were measured. As is shown in Fig. 3, the maximum intensity of the fluorescence is achieved by the use of 1.5 ml. of reagent solution, and as the reagent is added more and more, the intensity shows gradual decrease in proportion to its amount. For this reason 2 ml. of 1% 8-hydroxyquinaldine solution has been chosen as a suitable amount.

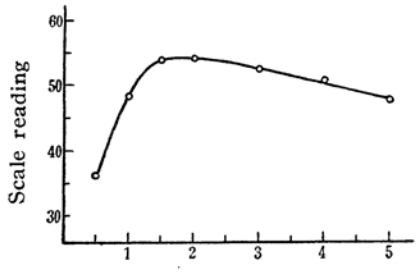

Fig. 3. Effect of amount of reagent.

Stability.—The fluorescence of the chloroform solution of beryllium chelate of 8-hydroxyquinaldine, stored in an amber glass bottle with a glass stopper and protected from sunlight was found to remain unchanged for a day, however, when the solution was left exposed to strong ultraviolet light, gradual decrease of fluorescence was observed.

Effect of Diverse Ions.—All of the ions which interfere with the spectrophotometric procedure mentioned in a previous paper[1], hinder this fluorometric method, therefore these ions should be absent. In this study, iron and aluminum were especially investigated, since they are most likely to exist together with beryllium. Their effects are shown in Table I. Though the effect of aluminum is not very great, it is desirable to remove more than 10 micrograms of aluminum.

TABLE I

EFFECTS OF IRON AND ALUMINUM

(Be taken in each case is 2.10 micrograms)

Added, Microgram		Fluorometer Scale Reading,	Be Found, Microgram
Fe	0	53.0	2.1_5
	5	47.5	1.8_7
	10	38.0	1.4_3
	15	30.5	1.0_8
	20	24.0	0.7_8
Al	5	51.9	2.0_8
	10	53.8	2.1_7
	25	58.7	2.4_0
	50	60.5	2.4_7
	100	62.0	2.5_5

The method to remove relatively large amounts of iron and aluminum from micro quantities of beryllium was made by the extraction separation method with oxine, mentioned in a previous paper[1], and then beryllium was determined fluorometrically. The results thus obtained are quite satisfactory, as shown in Table II.

TABLE II

THE FLUOROMETRIC RESULTS AFTER EXTRACTION SEPARATION WITH OXINE

Be Taken, Microgram	Metals Added, Milligram Fe	Al	Fluorometer Scale Reading,	Be Found, Microgram	Error, Microgram
0.00	20	—	7.5	0.0_0	0.0_0
0.00	—	20	13.0	0.2_6	$+0.2_6$
0.00	10	10	8.8	0.1_0	$+0.1_0$
0.53	10	10	20.0	0.6_0	$+0.0_7$
1.05	20	—	34.3	1.2_5	$+0.2_1$
1.05	—	20	32.5	1.1_8	$+0.1_3$
1.05	10	10	31.1	1.1_2	$+0.0_7$
2.10	20	—	49.7	1.9_8	-0.1_2
2.10	—	20	48.8	1.9_4	-0.1_6
2.10	10	10	52.5	2.1_0	0.0_0

Conclusion

The fluorometric method for determination of micro quantities of beryllium with 8-hydroxyquinaldine was established. By this method from 0.3 to 3 micrograms of beryllium in about 40 ml. of solution can be determined. The method of removing relatively large amounts of iron and aluminum from micro quantities of beryllium by the extraction separation method with oxine was also studied, and satisfactory results were obtained.

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