

Solvent Extraction of Beryllium as Acetylacetonate

Masayuki TABUSHI*

(Shigematsu Laboratory)

Received October 27, 1958

The solvent extraction of beryllium as acetylacetonate was studied. Beryllium acetylacetonate formed in nearly neutral solution was completely extracted with chloroform from the aqueous solution of pH 6~9. By the use of EDTA as a masking agent, the selectivity of acetylacetonate was enhanced, and beryllium could be separated from other metals by liquid-liquid extraction, although the extractibility of beryllium acetylacetonate was decreased slightly.

INTRODUCTION

Acetylacetonate forms the stable chelates with a number of metals and many of them are easily soluble in organic solvents such as chloroform, carbon tetrachloride, benzene *etc.*¹⁾ Under the appropriate condition, a given metal can be separated from others by solvent extraction as its acetylacetonate. Especially the selectivity of the reagent is so enhanced that acetylacetonate reacts with only uranium and beryllium, when ethylenediaminetetraacetic acid is used as a masking agent.²⁾ Therefore, in the presence of EDTA, acetylacetonate can be used for the separation, and in the same time for the determination of beryllium.

In the present paper, the detailed conditions for the quantitative extraction of micro amount of beryllium as acetylacetonate were described.

APPARATUS AND MATERIALS

Apparatus : Spectrophotometric measurements were made with a Hitachi Photoelectric Spectrophotometer Model EPU-2A, using 1.0 cm. silica transmission cells. A Horiba Glasselectrode pH-meter Model M-3 and a Metro EIT Scaler with GM-tube (TEN end window type, 132) was used for the measurements of pH and radioactivity, respectively.

Materials : Standard solution of beryllium ; 0.9819 g. of $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ was dissolved in water, and after adding 1 ml. of conc. H_2SO_4 , diluted to 50.0 ml. with water (1 mg. Be/ml.). The beryllium content was checked by 8-hydroxyquinoline gravimetric method. The stock solution was diluted to give a solution of 1.00 μg . per milliliter.

5 % acetylacetonate solution ; 25 g. of acetylacetonate was dissolved in water and diluted to 500 ml..

10 % EDTA solution ; 25 g. of disodium salt of ethylenediaminetetraacetic acid was dissolved in water, and diluted to 250 ml. with water.

0.1 % Eriochrome Cyanine R solution ; Dissolve 250 mg. of Eriochrome

* 田伏 正之

Solvent Extraction of Beryllium as Acetylacetonate

Cyanine R (ECCR) in water, and 1.25 g. each of sodium chloride and ammonium nitrate, 0.5 ml. of conc. HNO_3 and 25 ml. of ethanol, and then dilute to 250 ml. with water.

Chloroform ; CHCl_3 was washed by shaking with each volume of dil. NaOH solution, water, dil. HCl solution and three successive portions of water, and then distilled.

5 % sodium acetate solution.

Beryllium acetylacetonate ; the white precipitate of beryllium acetylacetonate was formed when solution of beryllium sulphate, containing excess of acetylacetonate was made ammoniacal. The precipitate obtained was twice recrystallized from hot ethanol and dried at room temperature. (The beryllium content in beryllium acetylacetonate was 4.32 % ; theoretical value is 4.34%, calculated from the formula $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$).

EXPERIMENTAL

1. Analytical Methods for the Determination of Beryllium

Eriochrome Cyanine R method and acetylacetonate method were used for the determination of beryllium

1. Eriochrome Cyanine R method. Eriochrome Cyanine R method was proposed by Hill³⁾. In order to apply the method to the sample containing acetylacetonate or EDTA, more detailed conditions were examined and the following procedures were developed as improved methods. The results in the present experiment agreed with the Hills's results but not entirely.

Procedure I : the sample solution, almost free from acid and salts, is pipetted into a 100 ml. beaker. Five milliliter of 5% sodium acetate solution, 1 ml. of 10 % EDTA solution and 5 ml. of 0.1 % ECCR solution are added. Adjust the pH to 9.7~9.8 with *N*-NaOH solution, transfer into 50 ml. measuring flask and dilute to the mark with water. Absorbance of the solution is measured at 510 $m\mu$ against the reagent blank.

Procedure II : Into the sample solution, 5 ml. of sodium acetate solution, 1 ml. of 10 % EDTA solution and 5 ml. of 0.1 % ECCR solution are added. For keeping the salt concentration at constant, 2.5 ml. of 5 *N* sodium hydroxide solution is added and the pH is adjusted to 9.7~9.8 with *N*- H_2SO_4 . Thereafter the solution is treated as mentioned in the procedure I.

The intensity of color, developed with ECCR, is effected with the concentration of salts and with that of EDTA present. Increase in the concentration of salts tends to increase the absorbance, but increase in the concentration of EDTA decreases the absorbance. Therefore the content of salts and the concentration of EDTA must be kept almost constant.

As acetylacetonate also prevent the formation of beryllium-ECCR complex, acetylacetonate which is used as the reagent for the separation of beryllium and extracted with organic solvent, must be decomposed. Beryllium acetylacetonate and excess acetylacetonate could be easily destroyed by fuming with perchloric

acid. Organic layer separated was dried and treated with perchloric acid, and then the above mentioned colorimetric procedures were carried out.

Because the values obtained by procedure II were often fluctuated, procedure I was used in the most experiments, although this was less sensitive than procedure II. When the determination of beryllium is carried out according to procedure I, perchloric acid used for the decomposition of organic matter must be evaporated as perfect as possible.

2. Acetylaceton method.⁴⁾ Procedure : Into the sample solution, add 1~2ml. of 10 % EDTA solution and 2.5 g. of sodium chloride and dilute to about 30 ml. Adjust the pH to 7~8, add 0.8 ml. of 5 % acetylaceton solution and adjust the pH again. The solution is transferred into a 100 ml. separating funnel, diluted to approximately 50 ml. and shaken with 20.0 ml. of chloroform. Organic layer is separated and washed with two 50 ml. portions of 0.1*N*-NaOH solution for the removal of excess acetylaceton, and dehydrated by adding a small amount of anhydrous sodium sulphate. Absorbance of the solution is measured at 295 m μ against the reagent blank. Manganese (II), Cr (III) and Ti (IV) interferes the determination of beryllium, but Ag, Al, Ba, Ca, Cd, Co, Cu (II), Fe (III), Mg, Mo (VI), Ni, UO₂ (II), V (V), W (VI) and Zn does not give any effect, if their quantities do not exceed 10 mg.

Beryllium acetylacetonate was dissolved in chloroform and the absorption spectrum was measured. As shown in Figs. 1 and 2, the spectrum of the Be-chelate (curve A in Fig. 1) is different from that of the reagent acetylaceton (curve A in Fig. 2). but acetylaceton shows so intense absorption at 295 m μ which is maximum wave length of the absorption band of Be-chelate, that the excess reagent must be removed.

When 20 ml. of chloroform solution of acetylaceton was stripped by 50 ml. of

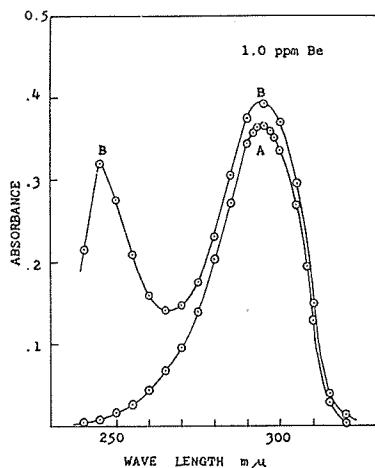


Fig. 1 Absorption spectra of beryllium acetylacetonate in chloroform
 A : Be-acetylacetonate in CHCl₃
 B : Be-chelate, extracted from aqueous solution according to the acetylaceton method (without EDTA ; measured against pure solvent)

Solvent Extraction of Beryllium as Acetylacetonate

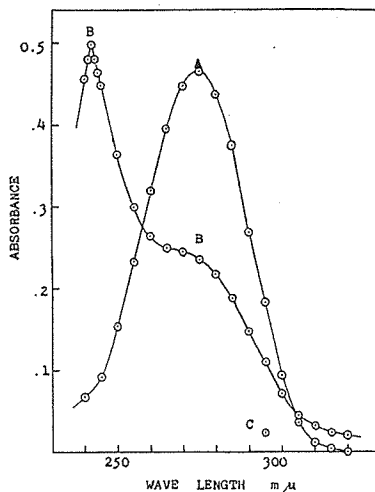


Fig. 2 Absorption Spectra of Acetylacetonate in Chloroform

A : Acetylacetonate in CHCl_3 , ca. $5 \times 10^{-5}\text{M}$.

B : 0.2% $(\text{CH}_3\text{CO})_2\text{CH}_2$ -chloroform solution, washed with $\times 2.5$ vol. of 0.1N-NaOH

C point : As value, obtained after more washings with 0.1N-NaOH

0.1 N-NaOH solution, the spectrum of the solution was deformed as shown by curve B in Fig. 2. And by shaking with more 50 ml. of 0.1 N-NaOH solution, absorbance at 295 $m\mu$ reduced to the point C in Fig. 2. However the successive washing did not reduce the absorbance of the blank solution. At the same time, the stripping effect on the spectrum of Be-chelate was examined, and it was confirmed that the beryllium acetylacetonate was stable in chloroform. Curve B in Fig. 1

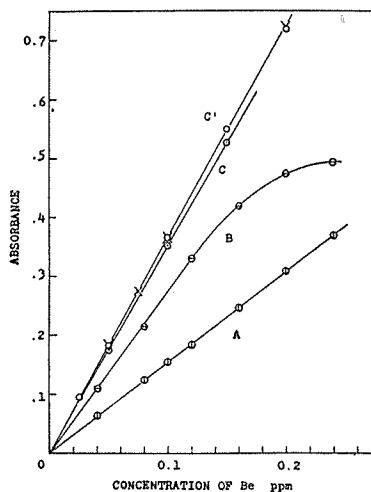


Fig. 3 Analytical curves for Be-ECCR method and -acetylacetonate method.

A : for Procedure I in ECCR method.

B : for Procedure II in ECCR method.

C : for Acetylacetonate method.

C' : for Acetylacetonate method without EDTA ; x points show As obtained from Be $(\text{C}_6\text{H}_7\text{O}_2)_2$ solution.

is the absorption curve of beryllium acetylacetonate which was extracted from aqueous solution according to the above mentioned procedure.

The analytical curves for ECCR method and acetylacetonate method were presented in Fig. 3. Curve C' in Fig. 3 was obtained by acetylacetonate method without the use of EDTA and sodium chloride. The x points which were the values for the solution of beryllium acetylacetonate in chloroform, fall on the same curve. This fact indicates that beryllium may be extracted quantitatively in the absence of EDTA. Moreover it can be seen that about 97% of beryllium may be extracted into chloroform layer, comparing with curve C and curve C'.

II. Extraction of Beryllium

1. Effect of concentration of acetylacetonate. The different amount of acetylacetonate was added to the solution containing 2 μ g. or 5 μ g. of beryllium. The pH was adjusted to 7.0~8.0 and solution was diluted to 50 ml. Beryllium acetylacetonate was extracted with 10ml. and two successive 5ml. portion of chloroform. Organic layer was separated, and evaporated in a beaker. The organic matters were decomposed with perchloric acid, and then the amount of beryllium was determined by ECCR method. On the other hand, extractions of beryllium acetylacetonate were made with 20.0 ml. of chloroform, and the concentration of beryllium in chloroform was determined by acetylacetonate method. As these extractions were made in the absence of EDTA, the curve C' in Fig. 3 was used for the analytical curve of acetylacetonate method.

Figure 4 shows the effect of the concentration of acetylacetonate on the extractibility of beryllium acetylacetonate.

2. Effect of pH value. The relation of extractibility of beryllium acetylacetonate in chloroform on the pH values of aqueous solution was investigated, using 1.0 ml. of 5% acetylacetonate solution. The result was presented in Fig. 5. As shown in this figure, beryllium acetylacetonate was extracted nearly quantitatively at a pH between 6.0 and 9.0.

3. Effect of ethylenediaminetetraacetic acid. Acetylacetonate forms the extractable chelate with many metal ions, but in the presence of EDTA as a masking agent, the extraction of other metals is inhibited, although the extraction of

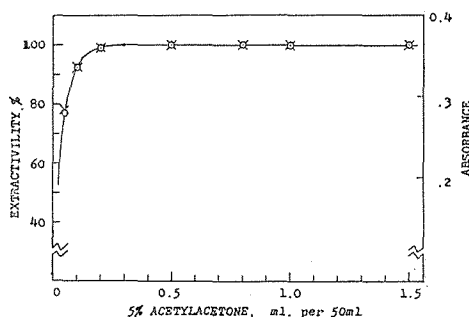


Fig. 4 Effect of acetylacetonate concentration.

-x- Extractivity, obtained by ECCR method.

-o- Absorbance, measured by acetylacetonate method (0.1 ppm Be).

Solvent Extraction of Beryllium as Acetylacetonate

beryllium is slightly affected.

The influence of EDTA was examined and the results are summarized in Table 1. The extraction recovery can be increased by addition of salts such as sodium chloride, sulphate and nitrate, but does not reach to 100 % in any case ; it reaches to a maximum value of 97.0 percent.

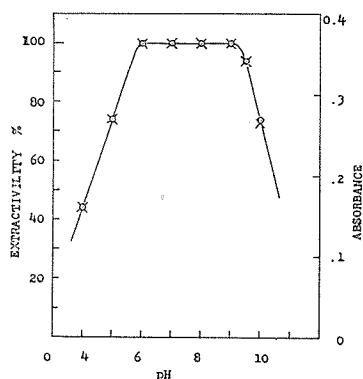


Fig. 5. Effect of pH.

-X- Extractivity, obtained by ECCR method.
 -O- Absorbance, measured by acetylacetonate method (0.1ppm Be).

Table 1. Effect of EDTA.

10% EDTA added	Salt added	Recovery*	Absorbance**
—	—	(100.0%)	0.366
0.2 ml.	—		0.300
0.5	—		0.298
1.0	—		0.297
2.0	—	91.4 %	0.289
1.0	1 g. NaCl	94.4	
//	// NaNO ₃		0.347
//	2.5 g. NaCl	96.8	0.352
//	// Na ₂ SO ₄	96.8	0.352
//	// NaNO ₃	96.4	0.350
2.0	// NaCl	96.8	0.352
15.0	// //		0.350

* Obtained by ECCR method.

** Measured at 295 mμ by acetylacetonate method, using 2.0 μg. of beryllium.

4. Effect of volume of solvent. Beryllium was extracted here with one 10 ml. portion of the solvent, instead of using 10+5+5 ml. In this case, the recovery of beryllium did not exceed 80 %, even when EDTA was absent. The principal reason for this result is not the incomplete extraction of the chelate, but the incomplete separation of organic layer. It is desirable that the extraction is followed by two or three successive portions of the solvent for the complete recovery of chloroform containing beryllium acetylacetonate. Therefore 10+5+5 ml. of chloroform was used for the procedure.

5. Procedure for the separation of beryllium. From the results, above mentioned the procedure for the separation of beryllium was developed as follows :

To the sample solution, add 2 ml. of 10% EDTA solution, 2.5 g. of NaCl and 1 ml. of 5% acetylacetone solution, adjust the pH of the solutions to 7.0~8.0 and dilute to about 50 ml. with water. Extract beryllium acetylacetonate by shaking with 10+5+5 ml. of chloroform. Ninety-seven percent of beryllium can be extracted by this procedure.

III. Separation of Beryllium from the Mixed Fission Product⁵⁾

The sample solutions containing 1 μ g. of beryllium and mixed fission product (radioactivity : *ca.* 50,000 cpm measured by G-M counter) were treated by the separation procedure, described in II. 5. The recovery of beryllium was 96.5 % and the radioactivity of extracted layer was only 5.0 ± 3.6 cpm (mean value of two experiments). So the decontamination factor is about 10^4 , and the separation of beryllium from the radioactivity of mixed fission product is complete.

SUMMARY

The separation of beryllium by liquid-liquid extraction as acetylacetonate was investigated.

Beryllium acetylacetonate was extracted nearly quantitatively with chloroform from the solution having pH value 6.0~9.0.

The use of EDTA as a masking agent, beryllium could be separated from the mixed fission product ; the recovery of beryllium was 97 % and the decontamination factor was about 10^4 .

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Professors M. Ishibashi and T. Shigematsu for their kind guidance and encouragement throughout the investigation.

REFERENCES

- (1) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," P. 158. Wiley, N. Y. 1957.
- (2) J. F. Steinbach and H. Freiser, *Anal. Chem.*, **25**, 881. (1953).
A. Krishen and H. Freiser, *ibid.*, **29**, 288 (1957).
- (3) U. T. Hill, *ibid.*, **30**, 521 (1958).
- (4) J. A. Akams, E. Booth and J. D. H. Strickland, *Anal. Chim. Acta*, **6**, 462 (1952).
T. Shigematsu and M. Tabushi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.)*, in press.
- (5) Recently, a radiochemical separation procedure has given by J. D. Buchanan [*J. Inorg. Nuclear Chem.*, **7**, 140 (1958)] for Be in the presence of mixed fission product and U. In this procedure, the decontamination was achieved by anion exchange, $\text{Fe}(\text{OH})_3$ scavenging, and by acetylacetone extraction.