

Solvent Extraction of Metal Acetylacetonates

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Received June 4, 1959

The extraction behaviours of metal acetylacetonates were described. Extraction curves were obtained by shaking the aqueous solution of metal salt, containing 1 % acetylacetone and having a various given pH, with 20 ml. of chloroform or of butyl acetate. Al, Be, Fe (III), Ga, Hf, In and UO₂ were almost quantitatively extracted with chloroform, and Fe, In and UO₂ were completely extracted also with butyl acetate. Ce, Cu, Pb, Mn, Y and Zn were extracted incompletely, and Cd, Co, Mg, Ni and Sr could not be extracted at any pH.

Effect of EDTA on the extractions was also investigated. By introducing EDTA, the selectivity of acetylacetone was enhanced. Al and Fe were extracted only a small part, and other metals was not extracted at all, although the extraction of Be and UO₂ were nearly quantitative.

From the summarized results, the application of the solvent extraction of metal acetylacetonate to the separation of metals was discussed.

INTRODUCTION

In order to establish a method for the separation and the spectrophotometric determination of metals by solvent extraction as its acetylacetonate, the author has already proposed the methods for beryllium¹⁾, uranium²⁾⁴⁾ and ferric iron³⁾⁵⁾. In the present paper, the extractions were carried out on acetylacetonates of fifteen metals, such as aluminium, cadmium, cerium, cobalt, copper, gallium, hafnium, indium, lead, magnesium, manganese, nickel, strontium, yttrium, and zinc. And the results were discussed, together with the results on beryllium, uranium and iron.

APPARATUS AND MATERIALS

Apparatus

Spectrophotometric, fluorometric and polarographic measurements were made with following apparatus.

Hitachi's photoelectric Spectrophotometer, Model EPU-2A, with 1.0 cm silica transmission cells.

A Shimadzu's Universal Fluorometer, Model UF-1.

A Yanagimoto's Polarograph, with a Polarorecorder, P.R.-2.

A Horiba's Glass electrode pH meter, Model M, and a Metro's EIT Scaler,

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Model 6E, with G-M. tube 132, were used for pH measurements and radioactivity countings.

Materials

5% Acetylacetone solution; 10% EDTA solution; 4.3% calcium chloride solution; chloroform and butyl acetate.

These solutions and organic solvents were prepared or purified as previously described¹⁾⁻⁵⁾.

Standard solutions of metals were prepared by dissolving pure metals or R.G. metal salts, which were weighed accurately. All reagents, used for the spectrophotometric, fluorometric or polarographic determinations were also reagent grade, and blank tests were carried out.

EXPERIMENTAL

I. Extraction Procedure

1) **Procedure A (Procedure for the use of radioactive isotopes as tracer).** Extractions were made as follows for cerium, cobalt, hafnium, nickel, strontium, yttrium and zinc.

To the solution of metal salt (about 30 ml.), 10 ml. of 5% acetylacetone solution were added*, and pH of the solution was made to a desirable value with *N* NaOH solution or *N* H₂SO₄ solution. The resulting solution was transferred into a 100 ml. separating funnel and diluted to 50 ml. with water. Twenty milliliters of chloroform or of butyl acetate were added, and the mixture was shaken until it attained the equilibrium.

After the separation of two layers, 4 ml. of aqueous layer or 2 ml. of solvent layer was pipetted into a stainless steel sample dish, and dried under an infrared lamp. Radioactivities of the samples were measured with a G-M scaler and compared with the standard, which was prepared by diluting the original solution in the same ratio as on the samples and was counted at the same geometry.

2) **Procedure B.** The extraction recoveries of other metals than the above ones, were determined spectrophotometrically (for copper, lead and manganese), fluorometrically (for aluminium, gallium and indium), polarographically (for cadmium) and chelatometrically (for magnesium). Procedure was designed as follows.

Addition of acetylacetone, control of pH value, and dilution were carried by the same manner as in the procedure A. Extractions were made with 10 ml. and two successive 5 ml. portions of organic solvents, which were combined in a beaker and evaporated. Organic matters were decomposed by fuming with perchloric acid, the residue was dissolved with water, and then the resulting solution was provided for the determination of metal ions.

* For the study on the effect of EDTA, 2 ml of 10% EDTA solution, with or without 5 g. of NaCl or 2 ml. of CaCl₂ solution, was added here.

II. Procedure for the Determination of Metals

1) **Aluminium**⁶⁾. To the sample solution, add 1.5 ml. of 0.1% Pontachrome blue black solution, 5 ml. of 10% NH_4Ac solution and a few milligram of hydroxylamine, adjust the pH to 4.7, and dilute to the mark in a 50 ml. volumetric flask. Heat the solution for 10 minutes at about 60°C, cool, and measure the fluorescence.

2) **Cadmium**. To the sample solution, add 10 ml. of 2*N* HCl solution and dilute to just 20 ml. Concentration of cadmium was then determined polarographically.

3) **Copper**. The sample solution was transferred into a 20 ml. volumetric flask, with 10 ml. of conc. HCl and with water, and then diluted to the mark. Absorbance was measured at 272 $m\mu$., against HCl (1 : 1). Effect of ferric impurity was corrected by the absorbance value, measured at 374 $m\mu$.

4) **Gallium**⁷⁾ To the solution, add small amount of hydroxylamine, 1 ml. of 1% 2-methyloxine solution (in *N* HAc) and 5 ml. of 20% NH_4Ac solution, dilute to about 50 ml. and adjust the pH to 3.9~4.1. Extract with 20+10+10 ml. of chloroform, combine the chloroform layers in a 50 ml. measuring flask, dilute to the volume with chloroform and dehydrate with anhydrous sodium sulphate. The intensity of fluorescence was measured.

5) **Indium**⁸⁾ Indium was determined by the same procedure as in the case of gallium, but the extraction was made at pH 5.5.

6) **Lead**⁹⁾ Procedure for the spectrophotometric determination of lead was the same as that for copper, except that absorbance was measured at 270 $m\mu$..

7) **Magnesium**. Magnesium was determined by the common EDTA titration, in which 0.002 *M* standard solution and a microburret were used for the semimicro amounts of the metal.

8) **Manganese**¹⁰⁾. To the sample solution, which was evaporated to almost dryness, add 2 ml. of perchloric acid (70%) and 10 ml. of water, and heat to boiling. Add 0.2~0.3 g. of potassium metaperiodate, and keep just under the boiling point for 15 minutes, with occasional stirring. Cool, dilute to 20.0 ml. and obtain the absorbance at 525 $m\mu$.

RESULTS AND CONCLUSION

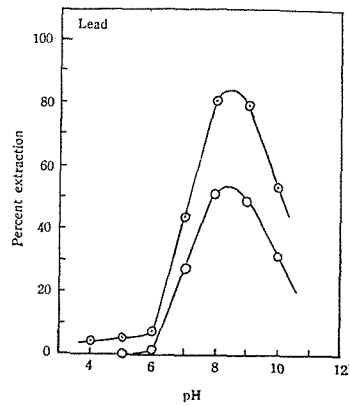
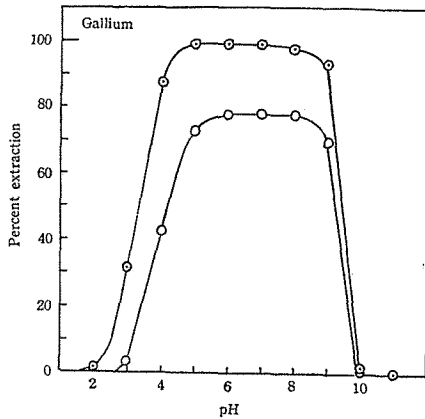
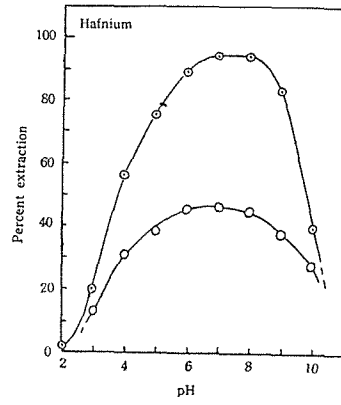
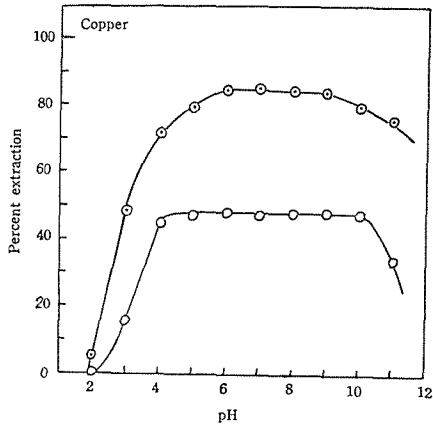
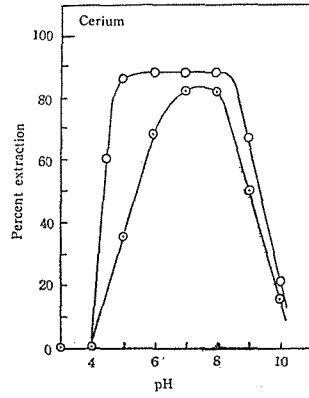
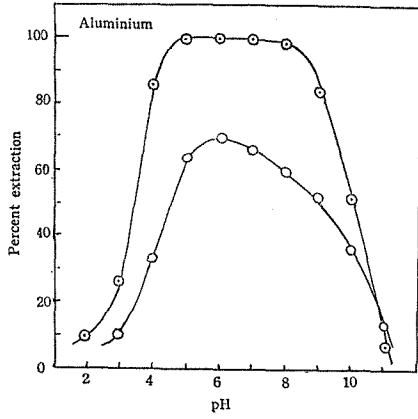
The results were shown in figures, as extraction curves, and the conditions for the extraction were summarized in Table I.

In general, chloroform seems to be much superior to butyl acetate for the extraction of metal acetylacetonates, except for the chelates of cerium, indium and uranium.

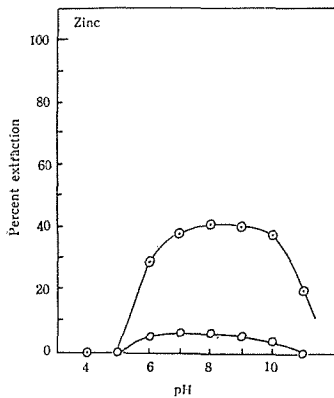
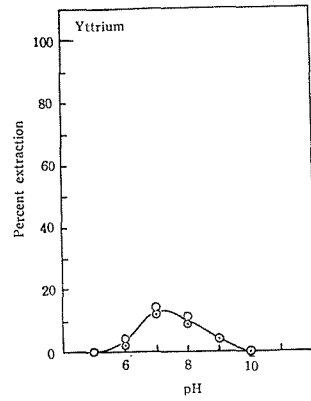
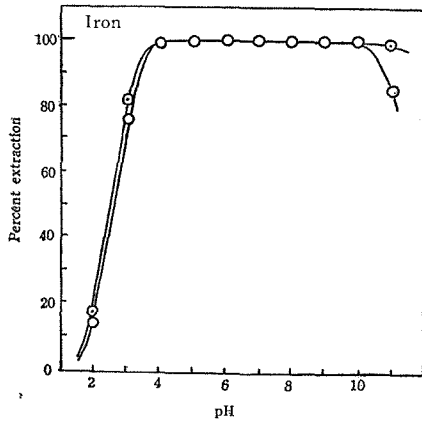
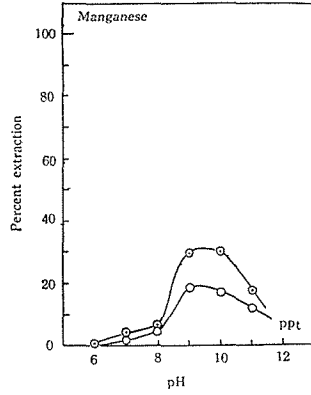
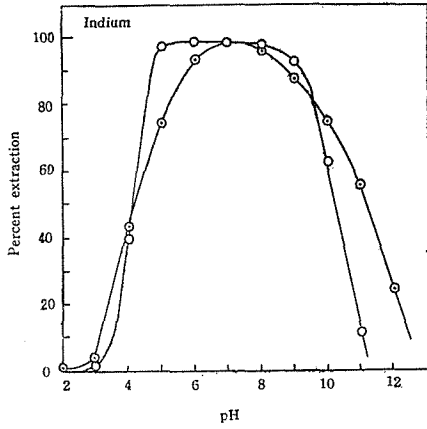
The extractions of aluminium-, gallium-, indium- and hafnium acetylacetonates are approximately quantitative, as well as beryllium-, uranium- and ferric iron chelates. On the other hand, cadmium, cobalt, magnesium, nickel and strontium can not be extracted at any pH value. The chelates of cerium, copper, lead, zinc and manganese can be extracted, but not completely.

On the extractable metals, the minimum values of pH for the quantita-

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Extraction curves of metal acetylacetonates



— ⊙ —
 Extracted with chloroform
 — ○ —
 Extracted with butyl acetate

Extraction curves of metal acetylacetonates

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tive extraction are larger than that obtained by the extraction with acetylacetonone or with acetylacetonone-chloroform (1 : 1) mixture. Such a phenomenon may be due to the low concentration of the reagent, acetylacetonone³⁾.

Table 1. Extraction recoveries of metal acetylacetonates.

Metal	Chloroform		Butyl acetate		pH	Reference	
	pH	% Extr.	pH	% Extr.		pH	% Extr.
Al	4.5—8	100	4.8—7	65—70	> 4	90—95	3)
Be	6—9	100*			5—10.5	100	1)***
	5—9.5	100			> 2	100	2)
Cd	2—12	<1	2—12	<1			
Ce	6.8—8	80—85	5—8.5	85—90			
Co	3—9	<1	3—9	<1	0—6	0	5)
Cu	5—10	80—85	4.5—10	45—50	> 2	85	2) 4)
Fe	4—11	100	4—10	100	1.5	100	5)
Ga	4.5—8	95—99	5.5—8.5	75—80	> 3	95	3)
Hf	6—8.5	90—95	5—8	40—45			
In	6—8	95—99	5—8.5	95—99	> 3	100	3)
Pb	8—9	80—85	8—9	50—55	7—8	75—85	4)
Mg	5—10	<1					
Mn	9—10	30	9—10	15—20	5.5—6.5	10—20	5)
Ni	3—9	<1	3—9	<1	0—6	0	5)
Sr	4—10	<1	4—10	<1			
UO ₂	6—7**	95**	5—7.5	93—100	> 3	95—100	4)
Y	6.5—8	10—12	6.5—8	10—15			
Zn	6.5—10	35—40	5—10	10	5.5—7	60	2)

* 2 ml. of 5% acetylacetonone solution were used.

** 20 ml. of the reagent were used.

*** Chloroform was used as an extracting solvent.

Other reference data were obtained by acetylacetonone-extractions.

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3) J. F. Steinbach and H. Freiser, *ibid.*, **26**, 375 (1954).

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5) J. P. Mckaveney and H. Freiser, *ibid.*, **29**, 291 (1957).

Table 2 represents the extraction yields, which were measured at pH 7, in the presence of 2 ml. of 10% EDTA solution, in the presence of EDTA and 5 grams of sodium chloride, or in the presence of EDTA and its equivalent of calcium chloride.

Extraction of beryllium is only slightly affected with EDTA. Extraction recovery is nearly quantitative in the high concentration of acetylacetonone (1%), and more than 90 percent of beryllium can be extracted even in the low concentration of the reagent (0.1%). In the latter extraction recovery can be increased by the addition of sodium chloride¹⁾.

Uranium is partially masked with EDTA, especially when chloroform is used as solvent. In this case, however, addition of sodium chloride gives the

Table 2. Extraction recoveries of metal acetylacetonates in the presence of EDTA.

Metal	Extraction recovery (%)			
	EDTA ^{a)}	Chloroform EDTA+NaCl ^{b)}	EDTA ^{a)}	Butyl acetate EDTA+CaCl ₂ ^{c)}
Al	7.1	10.0	10.6	12.2
Be	94.4 ^{d)}	96.0 ^{d)}		
	97—98	99.0		
Ce	<0.1	0.4	<0.1	0.37
Cu	1.2	1.0	0	9.8
Fe	4.7	9.0	1.5	14.7
Hf	0.1	0.1—0.2	0.1	0.1
Pb ^{h)}	0.7	1.5	0.7	0.5
Mn	<1	<1	<1	<1
UO ₂	10.0	31.5	34.5 ^{d)}	100 ^{d)}
	24.0 ^{e)}	81.6 ^{e)}	57.0	100
		92.5 ^{e,f)}		
	58.5 ^{e,f)}	92.5 ^{e,f)}		
		97.0 ^{e,f,g)}		
Y	<1.0	<2.0	<1.0	<2.0
Zn	0.2	0.3	0.2	0.28

5% Acetylacetone solution 10 ml. ; pH, 7.

a) 10% EDTA soln. 2 ml.

b) 5g. NaCl

c) 4.3% CaCl₂ soln. 2 ml.

d) 5% Acetylacetone soln. 2 ml.

e) 5% Acetylacetone soln. 20 ml.

f) 10% EDTA soln. 1 ml.

g) 10g. NaCl

h) pH 8

extraction recovery of 90 percent or more. And in the butyl acetate extraction, extraction yield can be recovered to quantitative by the addition of calcium chloride.

Iron and aluminium are masked with EDTA, but not perfectly. A few percent of the metals are extracted in the presence of EDTA, and extractabilities are somewhat increased by the addition of sodium chloride or of calcium chloride, although complete restoration can not be obtained. Gallium and indium might have a similar behaviour. Extraction recovery of these metals are affected by the relative value between the concentration of acetylacetone, concentration of a masking agent and concentration of metal ion itself.

Extractions of other metals investigated can be completely prevented by introduction of EDTA, and they are not extracted also in the presence of sodium chloride or of calcium chloride.

From the above experimental results, it seems to be possible, that the solvent extraction of metals as acetylacetonates is applied to the separation of metals, under the appropriate condition, *i.e.* by the use of a masking agent, or by the selection of pH value *etc.*

The author has already proposed some methods for the separation of metals,

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namely, beryllium from fission product¹⁾, uranium from fission product²⁾, uranium from thorium³⁾, and iron from nickel, cobalt, manganese³⁾, and uranium¹¹⁾.

SUMMARY

Extraction behaviours of metal acetylacetonates were investigated, using chloroform and butyl acetate as an extracting solvent.

Extraction curves were obtained with the chelates of many metals, such as aluminium, cerium, copper, gallium, hafnium, indium, iron, lead, manganese, yttrium, zinc *etc.*

The masking effect of ethylenediaminetetraacetic acid was also studied.

From the results, the applications of acetylacetonate-extraction to the separation of metals were discussed.

ACKNOWLEDGEMENT

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

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