

Title	Solvent Extraction of Iron with Chloroform as Acetylacetonate
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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1959), 37(4): 232-236
Issue Date	1959-11-25
URL	<a href="http://hdl.handle.net/2433/75722">http://hdl.handle.net/2433/75722</a>
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

# Solvent Extraction of Iron with Chloroform as Acetylacetonate

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*Received June 4, 1959*

The solvent extraction of ferric iron as acetylacetonate was studied. Ferric acetylacetonate was quantitatively extracted with chloroform from the aqueous solution, whose pH was in the range 4 to 9. Nickel, cobalt and manganese reacted with acetylacetonate to form the chelates, but the chelate of nickel and of cobalt could not be extracted at any pH, and manganese chelate was also not extracted in relatively low pH region. Therefore the solvent extraction of ferric acetylacetonate could be applied to the separation of iron from nickel, cobalt and manganese.

## INTRODUCTION

Ferric iron is extracted with organic solvents as its chelates or ion association complexes with cupferron, 8-hydroxyquinoline or with thiocyanate, chloride ion *etc.*<sup>1)</sup> Ferric acetylacetonate is also extractable chelate and was used for the exclusion of iron in the determination of magnesium by titan yellow method,<sup>2)</sup> or in the preparation of aluminium acetylacetonate.<sup>3)</sup> Recently McKaveney and Freiser<sup>4)</sup> studied on the condition in the acetylacetonate-extraction of iron. In these works, acetylacetonate was used as a solvent, in the mixture with carbon tetrachloride or with chloroform.

The author has studied the solvent extraction of metal-acetylacetonates, and reported the extraction of beryllium<sup>5)</sup> and of uranium<sup>6)</sup>, previously. In the researches, acetylacetonate was used as a chelating agent but not as an extracting solvent, because it is a relatively expensive reagent. In this case, as the chelation occurs in aqueous medium before the shaking with organic solvent, the extraction was rather easy, though pH range giving good extraction becomes to narrow, at low concentration of the reagent.

In this paper, the solvent extraction of ferric acetylacetonate was performed with chloroform, and the conditions were described.

## APPARATUS AND MATERIALS

### Apparatus

The measurements of pH values were made with Horiba's Glass electrode pH meter, Model M-3, and Metro's EIT Scaler Model 6E, with G-M tube (Kobe Kogyo's endwindow type 132, 1.68 mg/cm<sup>2</sup>) was used for radioactivity countings.

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## Materials

Ferric chloride solution ; a labelled ferric chloride solution\*, obtained from Oak Ridge National Laboratory, was diluted with 0.1 *N* hydrochloric acid to the solution giving appropriate radioactivity.

5% Acetylacetone solution ; 25 g. of acetylacetone were dissolved and diluted to 500 ml. with water.

Chloroform ; chloroform was purified as previously described.<sup>6)</sup>

## EXPERIMENTALS

### I. Determination of Extraction Recovery

Extraction recoveries of iron, cobalt and nickel were measured radiochemically by the use of their radio-isotopes. Extraction yield of manganese was determined colorimetrically by the permanganate method.

**Procedure for ferric iron.** After solvent extraction was carried out, chloroform layer was discarded. The aqueous layer was diluted to just 50 ml., 2 ml. or 4 ml. of the aliquote was pipetted into a stainless steel dish, 25 mm in diameter 7 mm in depth, and evaporated under a infrared lamp to complete dryness. Radioactivities were measured by G-M counter at a constant geometry and compared with a standard which was prepared by the same procedure but without extraction.

**Procedure for cobalt and nickel.** Organic layers combined in a beaker, after extraction, were transferred to a dish, little by little, and were all evaporated in it, and radioactivity was measured.

**Procedure for manganese.** Organic layers were evaporated and organic matters were decomposed by fuming with perchloric acid. After the residue was dissolved in a few milliliter of water, the permanganate method in which  $\text{KIO}_4$  was used as a oxidant, was adapted.

### II. Extraction of Iron

**1. Effect of concentration of acetylacetone.** Effect of concentration of acetylacetone was examined in the same manner as previously reported.<sup>6)</sup> Namely, 50 ml. of aqueous solutions containing different amount of the reagent were shaken with 10+5+5 ml. of chloroform, at pH 7.

Experimental results are presented in Fig. 1. Ferric acetylacetonate was very easily extracted as well as beryllium chelate,<sup>5)</sup> and quantitative extraction could be achieved when the concentration of the reagent was more than 0.05%.

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\* Labelled ferric chloride solution.

Description : Fe-55, 59 (P), Chemical form :  $\text{FeCl}_3$  in HCl solution (1.17 *N* acidic). Bach No. 190, Specific activity : 8.03 mc/g.

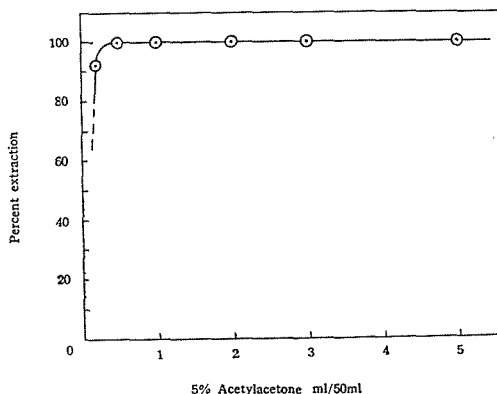


Fig. 1. Effect of concentration of acetylacetone.

**2. Effect of pH.** Effect of pH value on the extraction was investigated, using 2 ml. or 10 ml. of 5% acetylacetone solution. As shown in Fig. 2, ferric acetylacetonate was extracted quantitatively at a pH between 4.8 and 9.0 for the use of 2 ml. of the reagent (curve A) and between 4.0 and 10.5 for the use of 10 ml. (curve B), respectively. This pH region is identical with that in which ferric-acetylacetone system in aqueous medium shows a constant absorption spectrum. From the figure, it becomes evident that pH region giving good extraction expands when the concentration of the reagent increases.

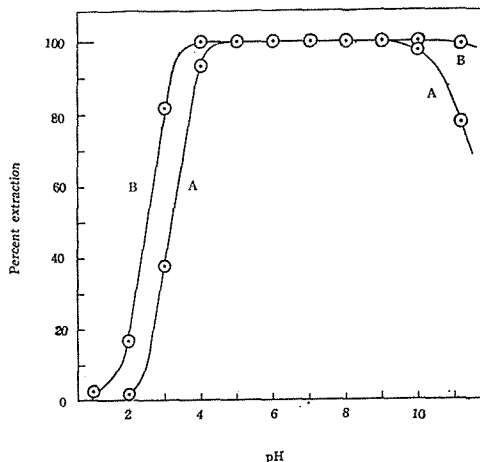


Fig. 2. Effect of pH value. (Extraction curves for ferric iron)

Concentration of acetylacetone anion is obtained from the following equation,

$$[R^-] = K_D \frac{[HR]}{[H^+]} = K_D \frac{(1-\alpha) C_R}{[H^+]}$$

where (HR) is concentration of acetylacetone in molecular form, and  $C_R$  is its total concentration,  $K_D$  and  $\alpha$  is dissociation constant and dissociation degree, respectively.

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At low pH, degree of dissociation,  $\alpha$ , is much less than unit, so (HR) is approximately equal to the total concentration,  $C_R$ . Therefore, to increase pH value by one unit and to make concentration of the reagent tenfold give a same effect. In Fig. 2, Curve B is displaced to the lower pH direction from curve A by about 0.7 unit of pH. This is approximately equivalent to fivefold concentration of the reagent.

3. **Procedure for the extraction of ferric iron.** From the above experimental results, the procedure for the extraction of iron was designed as follows.

To the sample solution, add 2 ml. of 5% acetylacetone solution, control pH of the solution to 6-8, and dilute to about 50 ml. Ferric acetylacetonate was extracted with 10 ml. and two successive 5 ml. portions of chloroform. By means of this procedure, ferric iron is completely extracted.

### III. Separation of Iron from Cobalt, Nickel and Manganese

Cobalt and nickel acetylacetonate can not be extracted at any pH, and manganese is incompletely extracted even at relatively high pH, if such an amount of acetylacetone as above mentioned is used. So the procedure for the extraction of iron may be successfully applied to the separation of iron from these metals. Kenny *et. al.*<sup>7)</sup> proposed a method for the preparation of carrier free Fe-59, where tracer level of iron was separated from irradiated cobalt, by means of xylene extraction as its acetylacetonate. In the present paper, the separation of iron from nickel and manganese as well as cobalt was investigated, using chloroform as an extracting solvent.

Extractions were made for the solutions containing a proper amount of cobaltous ion (Co-60 and carrier), nickel ion (Ni-63 and carrier) and manganese ion with about 1  $\mu$ g. of inactive ferric ion. Extraction recoveries of these ions were obtained by the procedure described in I., and the results are shown in Table 1.

Table 1. Extraction recovery of cobalt, nickel and manganese.

Metal	pH	Percent extraction
Cobalt	5.0	0.02
	7.0	0.12
	8.0	0.20
Nickel	5.0	0.05
	7.0	0.07
	8.0	0.07
	9.0	0.15
Manganese	5.0	0.5
	6.0	1.0
	7.0	4.5
	8.0	7.0
	9.0	30.0
	10.0	30.0

As shown in the table, for the separation from manganese, it is desirable to select pH value as low as possible, but from nickel and cobalt, pH value is not important, if it is controlled in a suitable range for extraction of iron.

chelate. When the complete extraction of iron is needed, chloroform seems to be better than xylene, because it has a specific gravity greater than 1, and so the treatment becomes much simpler.

#### SUMMARY

The solvent extraction of ferric iron as its acetylacetonate was investigated.

Ferric acetylacetonate was extracted quantitatively with chloroform from the solution having pH value 4-9.

As cobalt and nickel could not be extracted and manganese chelate was extracted only at higher pH value, iron could be separated from these cations. Only 0.1~0.01% of cobalt or nickel in the solution are accompanied with extracted ferric iron.

#### ACKNOWLEDGMENT

The author is grateful to Professors M. Ishibashi and T. Shigematsu for their kind guidance and encouragement throughout this research.

#### REFERENCES

- (1) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry" p. 212, Wiley, N. Y. 1957.
- (2) E. Abrahamiczik, *Angew. Chem.*, **61**, 96 (1949).
- (3) J. E. Steinbach and H. Freiser, *Anal. Chem.*, **26**, 375 (1954).
- (4) J. P. McKaveney and H. Freiser, *Anal. Chem.*, **29**, 291 (1957).
- (5) M. Tabushi, *This Bulletin*, **36**, 156 (1958).
- (6) M. Tabushi, *This Bulletin*, **37**, 226 (1959).
- (7) A. M. Kenney, W. R. E. Maton and W. T. Spragg, *Nature*, **165**, 483 (1950).