

Spectrophotometric Determination of Iron by Solvent Extraction as Acetylacetonate

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Spectrophotometric determination of iron, based on the extraction of ferric acetylacetonate, was studied. Ferric acetylacetonate was quantitatively extracted with butyl acetate at a pH value between 6 and 8. The chelate, in organic medium, exhibits three absorption maxima at 273, 353 and 438 $m\mu$., of which the last one was used for the determination. Colour was stable, Beer's law was obeyed in the range 0.5 to 10 ppm. of iron and molar extinction coefficient was about 3400 (L/M cm). Titanium, chromium and bismuth interfered by the precipitation of their hydroxides, and large amount of uranium and copper gave positive error, but many other metals did not interfere the determination.

INTRODUCTION

In the previous paper,¹⁾ the extraction method of ferric acetylacetonate with chloroform was investigated, using radioactive iron as a tracer. Ferric acetylacetonate shows absorption band in ultraviolet and in visible region, and it can be adapted to the colorimetric determination of iron, in organic medium as well as in aqueous solution. The colorimetric method used for the latter was already reported.²⁾ But in the aqueous medium, coloured metals, such as cobalt and nickel, interfere the determination of iron and so it seems to be better that solvent extraction is introduced. Absorption spectra of the chelate is affected by the concentration of excess acetylacetone in chloroform, but not in butyl acetate. Ferric acetylacetonate can be easily extracted with butyl acetate as well as with chloroform.

In the author's work, therefore, extractions were made with butyl acetate. The detailed conditions for the spectrophotometric determination of iron were described in the present paper.

APPARATUS AND MATERIALS

Apparatus

Spectrophotometric measurements were made with Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, using 1.0 cm. silica transmission cells. Hori-ba's Glass electrode pH meter, Model M, was used for the pH measurements.

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Materials

Standard solution of ferric perchlorate, 100 $\mu\text{g./ml.}$; the stock solution of ferric perchlorate was prepared as follows. Dissolve 500 mg. of electrolytic iron with perchloric acid by warming, oxidize by adding 30% hydrogen peroxide, evaporate the solution to nearly dryness, dissolve the residue with a few milliliter of perchloric acid and make up to 500 ml. with water. The stock solution was diluted to give the standard solution.

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

20% Ammonium acetate solution.

Butyl acetate and chloroform ; organic solvents were purified as previously described.^{3) 4) 5)}

Ferric acetylacetonate. The pure crystalline powder was obtained by the following procedure. To the aqueous solution of ferric perchlorate, excess of acetylacetone was added and then the solution was made ammoniacal. The resulting red precipitate of acetylacetonate was recrystallized twice from hot ethyl alcohol, and dried at room temperature. The iron content in the ferric acetylacetonate was 15.90% ; the theoretical value is 15.83%, calculated from the formula, $\text{Fe}(\text{C}_2\text{H}_7\text{O}_2)_3$.

EXPERIMENTAL

I. Absorption Spectra of Ferric Acetylacetonate in Organic Solvent

In order to survey previously the characteristics of ferric acetylacetonate, the absorption spectra of the chelate solutions which were prepared by dissolving the crystal, were measured. Spectra obtained in butyl acetate medium were shown in Fig. 1. Curve A (for $2 \times 10^{-5} M$) and curve B (for $1 \times 10^{-4} M$) were obtained with the solution, which did not contain excess acetylacetone, and they have three absorption maxima at 273, 353 and 438 $m\mu$. Spectra of the solutions, containing excess reagent, were then measured against each reagent blank, and it was confirmed that the excess of acetylacetone did not affect on the spectra, except in the shorter wave length region, in which acetylacetone showed large absorption.

In chloroform, spectra of the chelate gave similar shape and have also three maxima, as presented by curve A (for $1 \times 10^{-5} M$) and curve B (for $1 \times 10^{-4} M$) in Fig. 2, but in this case, excess of acetylacetone gave effect to increase absorbances. Curve C, obtained in the presence of 4% acetylacetone, does not fall on curve B. Such a phenomenon had been seen in the case of uranyl acetylacetonate, and so butyl acetate is much better for analytical purpose than chloroform.⁵⁾ Therefore in further experiments, butyl acetate was used as the extracting solvent.

Extraction of ferric chelate was carried out according to the following procedure, and absorption spectrum was measured against the reagent blank, which was shown in Fig. 3.

Spectrophotometric Determination of Iron by Solvent Extraction as Acetylacetonate

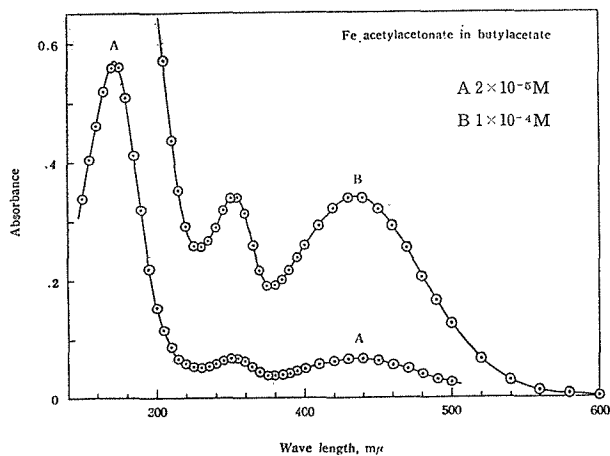


Fig. 1. Absorption spectra of ferric acetylacetonate in butylacetate.

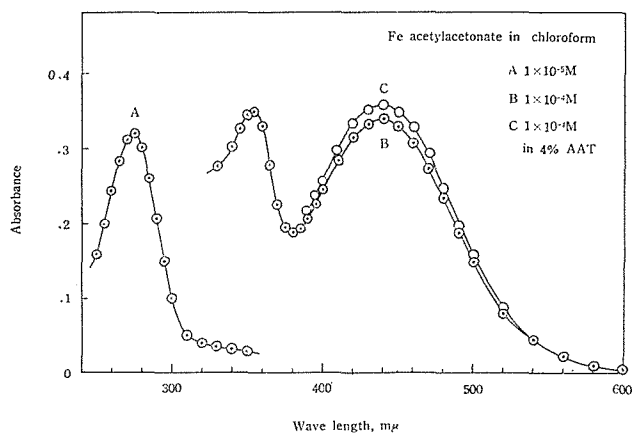


Fig. 2. Absorption spectra of ferric acetylacetonate in chloroform.

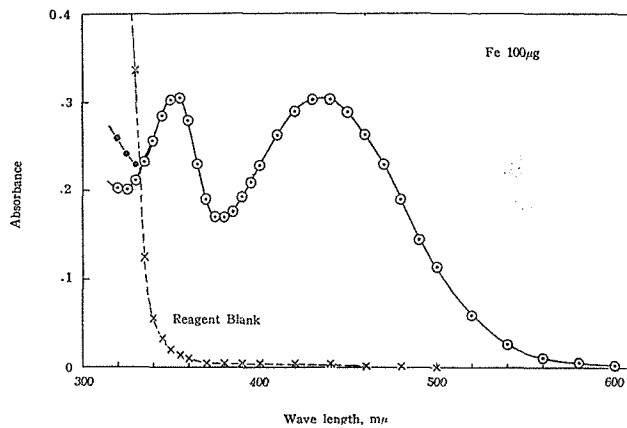


Fig. 3. Absorption spectrum of ferric acetylacetonate, extracted.

To the solution of ferric perchlorate (containing 100 μg . of ferric iron), 20 ml. of 5% acetylacetone solution was added, and its pH was adjusted to 7.0. After diluted to about 50 ml., ferric acetylacetonate was extracted by shaking with 20.0 ml. of butyl acetate for about one minute.

As shown in the figure, not only the form of the spectrum is quite similar to that of curve B in Fig. 1, but also, the curve which was calculated from the latter, falls on the former. This indicates that the species extracted, is (1 to 3) chelate, and the extraction of ferric iron is approximately quantitative.

II. Effect of Concentration of Acetylacetone

Different amounts of 5% acetylacetone solution were added to the sample solution, containing 100 μg . of iron, whose pH and volume were thereafter adjusted to 7.0 and 50 ml., respectively. Ferric acetylacetonate was extracted with 20.0 ml. of the solvent, and absorbance was measured at 440 $\text{m}\mu$. against reagent blank.

As shown in Fig. 4, it is not an important problem to keep the reagent concentration at constant, if it is more than 0.05%.

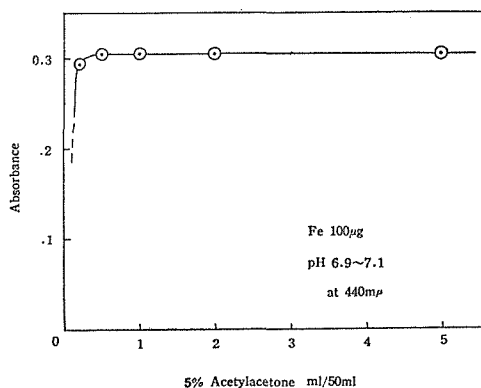


Fig. 4 Effect of concentration of acetylacetone.

III. Effect of pH Value

For the study on the effect of pH, ferric acetylacetonate was extracted from the solutions which contained 100 μg . of iron and 2 ml. of 5% acetylacetone solution, at various pH values.

Fig. 5 indicates that the constant absorbance is obtained at a pH between 4.0 and 9.0.

IV. Effect of Ammonium Acetate

In order to make pH control easy, it was attempted that ammonium acetate was used as a buffer solution. Ferric acetylacetonate was extracted in the presence of 5 ml. of 20% ammonium acetate solution, and its absorption curve agreed with that obtained in the absence of ammonium acetate.

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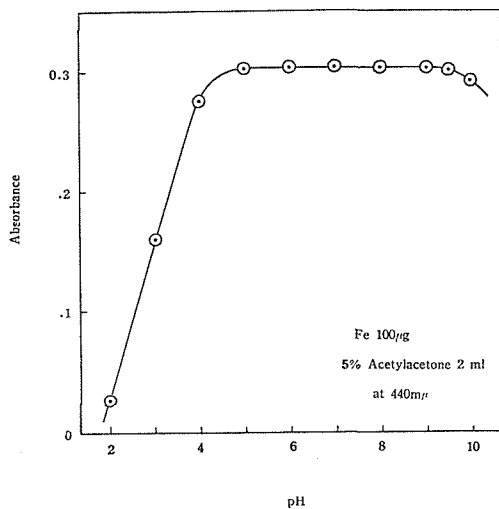


Fig. 5. Effect of pH value.

In the practical procedure, the adjustment of pH value may be replaced by adding a few milliliter of 20% ammonium acetate solution, if the sample solution does not contain large amount of mineral acid.

V. Analytical Procedure and Analytical Curve

From the above described results, the procedure for the spectrophotometric determination of ferric iron was designed as follows.

Into the sample solution, containing 10~200 μ g. of iron, add 2 ml. of 5% acetylacetonone solution, adjust the pH to 6~8*, and dilute to about 50 ml. with

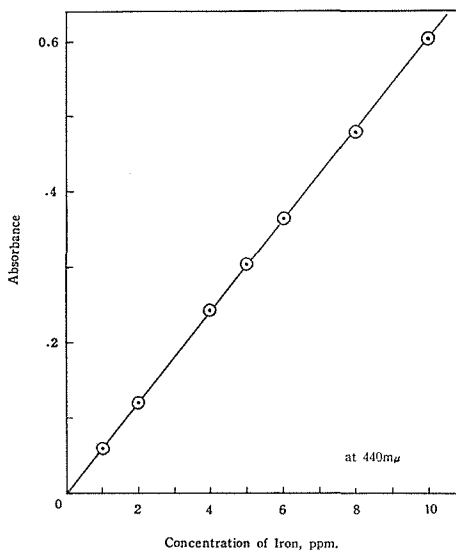


Fig. 6. Calibration curve.

* Ammonium acetate solution may be added here.

water. Transfer the resulting solution to a 100 ml. separating funnel and shake with 20.0 ml. of butyl acetate. Discard aqueous layer, dehydrate solvent layer with anhydrous sodium sulphate, and obtain absorbance at 440 $m\mu$. against the reagent blank or pure solvent.

Analytical curve is presented in Fig. 6. Beer's law is valid from 0.5 to 10 ppm., and molar extinction coefficient of ferric acetylacetonate is about 3400 ($L/M\text{ cm.}$) at 440 $m\mu$.

VI. Diverse Ions

Many metal ions react with acetylacetone to form the extractable chelates, but much of them is colourless. Therefore, the influence of the diverse ions was examined mainly on coloured metal ions, or on the metals which were anticipated to form coloured acetylacetonates.

Results were summerized in Table 1.

Table 1. Influence of diverse ions.

Name	Diverse ion added (mg.)	as	Fe found* ($\mu\text{g.}$)	Remark
Co ⁺⁺	10	sulphate	100.4	
Cu ⁺⁺	2	sulphate	108.0	
Mn ⁺⁺	10	sulphate	113	
	2		102	
	10		99.4	a)
Mo ⁶⁺	10	Na molybdate	100.4	c)
Ni ⁺⁺	10	sulphate	99.7	
U ⁶⁺	5	UO ₂ nitrate	151	
	5		138	b)
	1		107	
	1		104	a)
	1		101	b)
V ⁵⁺	10	NH ₄ metavanadate	98.7	c)
W ⁶⁺	10	Na tungstate	98.7	c)

* Fe present 100.0 $\mu\text{g.}$

a) Extractions were made at pH 5.

b) Extractions were made at pH 9.

c) 3 ml. of 5% acetylacetone solution were added.

Titanium (IV), chromium (III) and bismuth (III) interfered owing to the formation of hydroxide, and uranyl uranium, manganese and copper (more than five times of iron) gave positive error.

As manganese was not extracted at lower pH range, its interference could be avoided, when the extraction was made at pH 5. Uranyl acetylacetonate in butyl acetate has absorption maximum at 365 $m\mu$., so its interference can be deducted. Further paper will deal with the spectrophotometric method for the simultaneous determination of iron and uranium.

SUMMARY

A spectrophotometric method for the determination of iron was described. In which ferric iron was extracted with butyl acetate as its acetylacetonate. Effect of the reagent concentration, pH value and ammonium acetate buffer, and influence of diverse cations were examined. Titanium, chromium and bismuth, and large amounts of copper interfered the determination of iron.

ACKNOWLEDGEMENT

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