Solvent Extraction-spectrometric Determination of Iron(III) with Mixture of Dibenzoylmethane and Tri-n-octylphosphine Oxide

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Synopsis

A method for the spectrophotometric determination of iron(III) utilising the synergistic extraction with dibenzoylmethane(DBM) and tri-n-octylphosphine oxide(TOPO) is described. Iron(III) can be extracted quantitatively into carbon tetrachloride or benzene with the mixture of DBM and TOPO at the wide pH range from 2.5 to 5.0. The extracted orange complex has an absorption maximum at 410 nm and the sensitivity for $\log(I_0/I) = 0.001$ is 3.8×10^{-3} μg Fe(III) cm^{-2}. The extracted species is probably Fe(III)(DBM)$_2$(TOPO). The linear calibration curve through the point of the origin was obtained up to 4.0 μg ml^{-1} of iron(III). The method is free of interference from iron(II) because it is not extracted into an organic phase. Of 37 foreign ions examined, thorium, uranium and titanium(IV) interfered seriously. This method was successfully applied to the determination of trace iron(III) in tap water and Mohr's salt, and is also applicable to the consecutive determination of iron(II) and iron(III).

Introduction

The β-diketones are well known as organic reagents for the solvent extraction and the spectrophotometric determination of many heavy metals. Acetylacetone and thenoyltrifluoroacetone are the representative ones which have been extensively used as analytical reagents. Dibenzoylmethane(DBM) is also one of the most important reagent of the β-diketones and has been sometimes used for the determination of trace iron.[1-4] This time, the authors have examined the reaction of iron(III) and DBM and found that, in the presence of tri-n-octylphosphine oxide(TOPO), iron(III) can be extracted with DBM for shorter time without heating and at wider pH range of aqueous solution than the case of the absence of TOPO.[1] The extracted iron(III) can be determined spectrophotometrically with more sensitive than the methods using the common reagents for iron, such as 1,10-phenanthroline,[5] 2,2'-bipyridine[5] and 8-hydroxyquinoline.[6,7] In this method, moreover, iron(II) and iron(III) can be separated from each other since iron(II) is not extracted into the organic phase under the extraction conditions of iron(III). This facilitates the determination of trace iron(III) in large amount of iron(II) and the consecutive determination of iron(II) and iron(III). A lot of methods for the consecutive spectrophotometric determination of iron(II) and iron(III) have been reported by now.[8-21] But, of these, the methods which can be utilised for the separation of iron(II) and iron(III) like the

method proposed here are only a few. In the majority of these methods, iron(II) and iron(III) can not be separated from each other and are determined by the measurements of both total iron and either iron(II) or iron(III). This paper describes the fundamental conditions for the solvent extraction-spectrophotometric determination of iron(III) with DBM in the presence of TOPO and for the consecutive determination of iron(II) and iron(III).

Experimental

Apparatus

A Shimazu UV-2100 spectrophotometer with 1 cm quartz cells and a Hitachi 170-10 flame atomic absorption spectrometer were used for the absorbance measurements and a Hitachi-Horiba model M-5 glass electrode pH meter for the pH measurements. For the shaking of solutions, an Iwaki KM type shaker was used.

Reagents

All chemicals were of analytical-reagent grade.

　　Standard iron(II) solution. An iron(II) solution was prepared fresh each day by dissolving ferrous ammonium sulfate hexahydrate (Mohr's salt) in diluted sulfuric acid to a required concentration gravimetrically.

　　Standard iron(III) solution. A solution containing about 1 mg ml^{-1} of iron(III) was prepared by dissolving iron(III) nitrate in a small amount of nitric acid and diluting with distilled water. The iron(III) concentration was determined by the complexometric back titration with a standard thorium solution using Xylenol Orange as an indicator. This solution was diluted as required.

　　DBM solution. A 0.5% m/v DBM solution was prepared by dissolving a weighed amount of DBM in carbon tetrachloride which was synthesised by a conventional method and purified by the recrystallisation from methanol.[22]

　　TOPO solution. A 2% m/v TOPO solution was prepared by dissolving a weighed amount of TOPO (Dojindo Laboratories) in carbon tetrachloride.

　　A 1 mol dm^{-3} sodium acetate-1 mol dm^{-3} hydrochloric acid buffer solution was used for the pH adjustments.

Recommended Procedure

A sample solution (10-300 ml) containing up to 40 μg of iron(III) is transferred to a separatory funnel and the pH of the solution is adjusted to between 3.0 and 4.0 with 5 ml of buffer solution. Then, 10 ml of a carbon tetrachloride solution containing 0.25% m/v DBM and 1% m/v TOPO is added. After shaking the separatory funnel for 25 min and separating the phases, the organic phase is dried with unhydrous sodium sulfate and the absorbance is measured at 410 nm against the reagent blank as a reference.

Results and Discussion

Absorption Spectra

The absorption spectra of the iron(III) complex extracted into carbon tetrachloride by the recommended procedure and the reagent blank are shown in Fig.1. The organic phase contained the iron(III) complex has an absorption maximum at 410 nm, while the reagent blank does not show appreciable absorbance at this wavelength.

Choice of Synergists

The effect of some synergists on the iron(III) extraction were examined, adding various amounts of them into the organic phase. As shown in Fig. 2, the quantitative extraction of iron(III) became possible by the addition of TOPO or triethanolamine(TEA), resulting the highest absorbance of the organic phase.

Fig.2. Effect of the concentration of synergists on the extraction of iron(III) (20 μg) with 10 ml of carbon tetrachloride containing 0.25% m/v DBM and synergists. Synergists: (1), TOPO; (2), TEA; (3), TBPO; (4), TPP; and (5), TBP
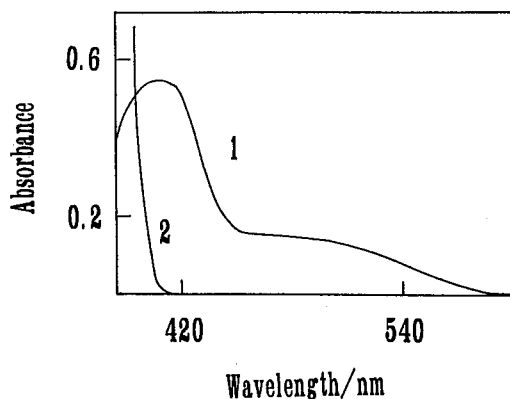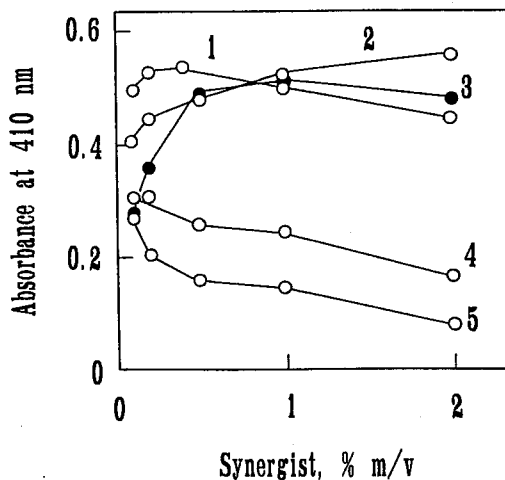
Fig.1. Absorption spectra of (1) iron(III) complex extracted at pH 4.0 with 10 ml of carbon tetrachloride containing 0.25% m/v DBM and 1% m/v TOPO from aqueous solution containing 20 μg of iron(III) and (2) reagent blank. Reference: (1), reagent blank; and (2), carbon tetrachloride
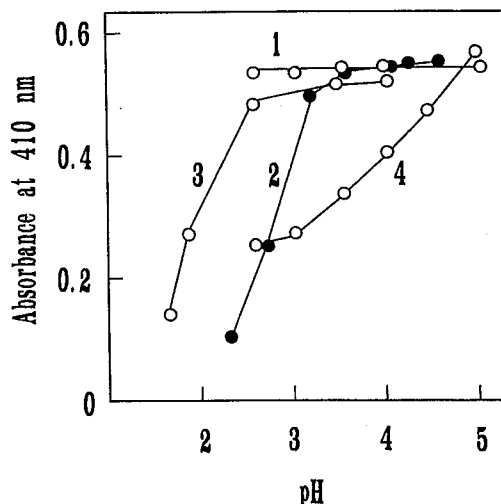
Fig.3. Effect of pH on the extraction of iron(III) (20 μg) with 10 ml of carbon tetrachloride containing 0.25% m/v DBM and synergists. Synergists: (1), 1% m/v TOPO; (2), 2% m/v TEA; (3), 1% m/v TBPO; and (4), the absence of synergist

Tri-n-butylphosphine oxide(TBPO) also gave relatively high absorbances, but these were a slightly lower than the case of TOPO or TEA. The presence of triphenylphosphate(TPP) and tributylphosphate(TBP), on the other hand, did not improve the extractability of iron(III) and the absorbances decreased gradually with a increasing the adding amount of them. Figure 3 shows the effect of pH of the aqueous phase on the extraction in the presence of TOPO, TEA or TBPO and in the absence of the synergist. The pH of the aqueous phase was measured only before the extraction as the differences of the pH values between before and after extraction were negligibly small. From the figure, it can be seen that iron(III) was not extracted quantitatively in the absence of the synergist, and that the presence of TOPO was the most favorable as it gave the widest pH range, 2.5-5.0, in which the maximum and almost constant absorbances were obtained. When the extraction was carried out above pH 5, on the other hand, the absorbance varied widely decreasing its value regardless the presence or the absence of the synergist. From these results, the extraction of iron(III) was carried out within the pH range from 3.0 to 4.0 using TOPO as a synergist.

Choice of Diluents
Several organic solvents, such as carbon tetrachloride, benzene, cyclohexane, n-butyl acetate and methyl isobutyl ketone(MIBK), were examined for the extraction of iron(III). Of these, carbon tetrachloride and benzene were found to be the most suitable solvents because of the high extractability and their satisfactory phase separation. In both solvents, moreover, the color intensity of the complex remained almost constant up to a volume ratio of the organic to the aqueous phase 1:30. The other solvents were found to be unsuitable for the extraction owning to low absorbance. In this experiment, carbon tetrachloride was mainly used because this solvent comes lower phase giving a simpler operation for the consecutive determination of iron(II) and iron(III).

Effect of DBM Concentration and Other Variables
Various concentrations of DBM in carbon tetrachloride were examined for the extraction of 20 μg of iron(III). The maximum and almost constant absorbances were obtained over the DBM concentration region from 0.1 to at least 0.5% m/v. The quantitative extraction of iron(III) could be achieved by shaking more than 25 min. The extract was very stable and the absorbance remained constant for at least 60 min after the extraction. The examination of the effect of 1 mol dm^{-3} sodium acetate-1 mol dm^{-3} hydrochloric acid buffer solution showed that the addition of 3-15 ml of this solution had no effect on the color intensity of the iron(III) complex.

Calibration Curve
Under the conditions described in the recommended procedure, Beer's law is obeyed up to 40 μg of iron(III) in 10 ml of carbon tetrachloride. The sensitivity of the determination was 3.8×10^{-3} μg Fe(III) cm^{-2} for $\log(I_0/I) = 0.001$ and the reproducibility of this method, expressed by the

relative standard deviation(RSD) of the absorbances which were obtained from five repeat determinations, was 1.1% for 300 ml of sample solution containing 20 μg of iron(III).

Interferences

The influence of foreign ions on the determination of 20 μg of iron(III) was examined. The results obtained were summarised in Table 1. Iron(III) could be determined within 5% errors in the presence of 1 mg each of 22 ions such as alkali metals, alkaline earth metals, aluminium, lead, zinc, cadmium, lanthanoids, chromium(VI), manganese(II), cobalt and nickel. When iron(III) was determined in a stream of nitrogen, moreover, iron(II) did not interfere even if 10 mg of it was coexisted. Thorium, uranium and titanium(IV), however, interfered seriously even present in only a small amounts.

Composition of the Complex

From Figs. 4 and 5, the mole ratio of iron(III) to DBM in the presence of TOPO is estimated to be 1:2, because maximum point of the continuous variation plots locates on about 0.33 of $[Fe(III)]:\{[Fe(III)]+[DBM]\}$ and a curve obtained by plots of log D (logarithm of distribution ratio of iron(III)) against pH shows a slope of about 2. As shown in Fig. 6, moreover, the plots of log D against logarithm of the concentration of TOPO in carbon tetrachloride show a linearity with a slope of about 1. From these results, it seems that the mole ratio of iron(III), DBM and TOPO is probably 1:2:1.

Table 1. Effect of foreign ions on the determination of 20 μg of iron(III)

Ion	Amount added/ μg	Fe(III) found/ μg	Ion	Amount added/ μg	Fe(III) found/ μg
Li⁺	1000	20.0	Th⁴⁺	20	21.4
K⁺	1000	19.9	V(V)	100	20.1
Mg²⁺	1000	20.3	Sn⁴⁺	20	19.4
Ca²⁺	1000	20.3	Cr³⁺	20	20.4
Sr²⁺	1000	20.1	Cr(VI)	1000	20.6
Ba²⁺	1000	20.0	Mo(VI)	20	20.2
Al³⁺	1000	20.3	W(VI)	20	19.4
Ga³⁺	20	20.4	UO₂²⁺	20	21.8
In³⁺	100	20.7	Mn²⁺	1000	19.9
Pb²⁺	1000	19.2	Fe²⁺	10000*	20.3
As(V)	1000	20.0	Fe²⁺	1000*	20.1
Bi³⁺	1000	20.0	Co²⁺	1000	20.0
Cu²⁺	20	20.2	Ni²⁺	1000	20.0
Zn²⁺	1000	19.7	Pd²⁺	1000	20.2
Cd²⁺	1000	20.1	Pt(IV)	1000	20.2
Y³⁺	1000	19.9	PO₄³⁻	40	20.3
La³⁺	1000	20.1	SO₄²⁻	1000	19.6
Ce³⁺	1000	20.8	F⁻	40	19.9
Ti(IV)	20	14.4	Tartrate	40	19.0

* Extraction was carried out in a stream of nitrogen.

Determination of Iron(III) in Tap Water

The proposed method was applied to the determination of iron(III) in tap water. The samples were filtered through a Toyo Roshi TM-2p membrane filter (pore size 0.45 μm) as soon as possible after sampling, and acidified with hydrochloric acid to about pH 2 for storage. As summarised in Table 2, the results obtained by the proposed method (the calibration method

and the standard addition method) and the flame atomic absorption spectrometry were in good agreement with each other.

Consecutive Determination of Iron(II) and Iron(III)

In this method, iron(II) is not extracted into the organic phase under the extraction conditions of iron(III). As a result, both iron(II) and iron(III) can be easily separated from each other. Utilising this, the consecutive determination of iron(II) and iron(III) was tried. The procedure of the determination is as follows.

According to the recommended procedure, first, only iron(III) is brought into the organic phase from the sample solution containing iron(II) and iron(III) by the extraction in a stream of nitrogen and determined. Then, iron(II) remained in the aqueous phase
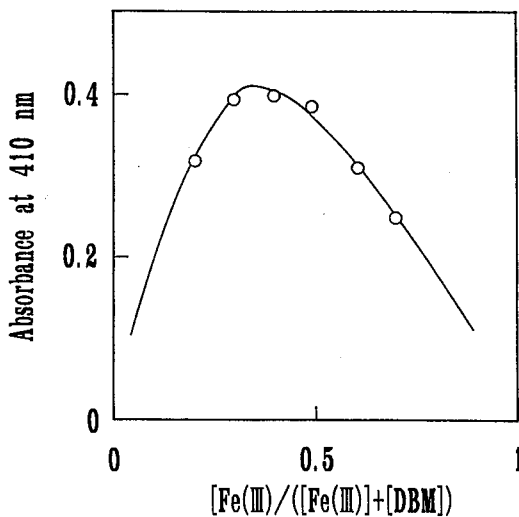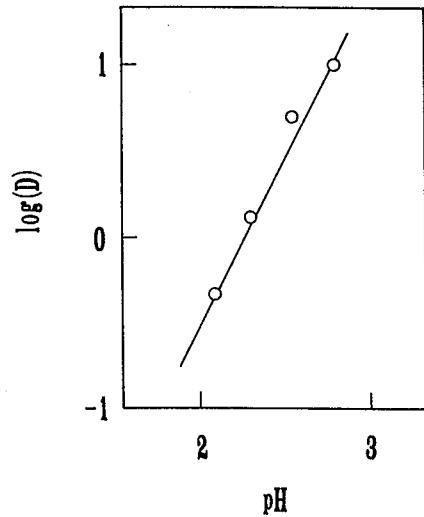
Fig.5. Relationship between pH and the distribution ratio(D) of iron(III). Organic phase, 10 ml of carbon tetrachloride containing 0.01 mol dm^{-3} DBM and 0.03 mol dm^{-3} TOPO

Fig.4. Mole ratio of iron(III)-DBM complex determined by continuous variation method at pH 3.0. [Fe(III)] + [DBM] = 1.76 × 10^{-6} mol dm^{-3}; organic phase, 10 ml of carbon tetrachloride containing 1% m/v TOPO
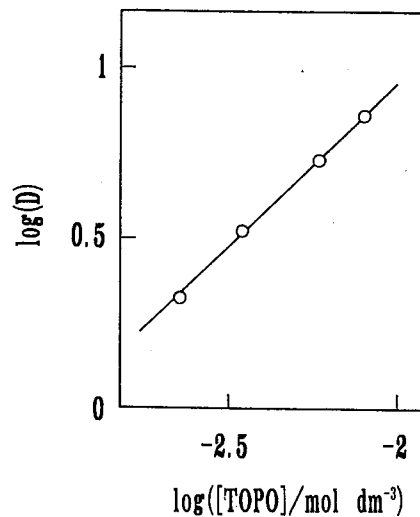
Fig.6. Relationship between the concentration of TOPO and the distribution ratio(D) of iron(III) at pH 3.0. Organic phase, 10 ml of carbon tetrachloride containing 0.25% m/v DBM

Table 2. Results of the determination of iron(III) in tap water

Location of tap water[+]	Sample volume/ ml	volume of organic phase/ ml	Fe(III) found/ng ml^{-1}*		
			Calibration method	Standard addition method	Flame AAS
Marunouchi	100	5	25.0	27.0	27.7
	200	10	29.0	25.0	27.7
	200[‡]	10	—	50.9	47.2
Kodatsuno	100	5	62.0	64.0	62.9
	200	10	60.0	65.3	62.9
Nonoichi	100	5	15.8	15.5	14.5
	200	10	18.0	17.2	14.5

* Average of duplicate determinations.

[+] Vicinity of Kanazawa city.

[‡] Sampling date is different.

Table 3. Results of the consecutive determination of iron(II) and iron(III) for synthesised samples

Sample No.	Fe taken/ μg		Fe found/ μg		
			Spectrophotometry		Flame AAS
	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(II)
1	10.0	5.0	10.0	5.0	5.1
2	10.0	10.0	10.0	10.2	10.2
3	10.0	15.0	10.0	15.1	15.0
4	10.0	20.0	10.0	19.7	20.0
5	5.0	10.0	4.9	10.2	10.0
6	10.0	10.0	10.0	9.8	10.0
7	15.0	10.0	14.9	10.0	10.0

Table 4. Results of the determination of iron(III) in Mohr's salt

Sample No.	This method		Mohr's method	
	Sample taken/ mg	Fe(III) found*, %	Sample taken/ g	Fe(III) found[+], %
1	5.0	0.022	1.0	0.019
	10.0	0.024		
2	5.0	0.073	1.0	0.061
	10.0	0.063		

* Average of two replicate determinations.

[+] Average of three replicate determinations.

is oxidised to iron(III) by the addition of 4 ml of about 3% m/m hydrogen peroxide and determined spectrophotometorically according to the recommended procedure, or iron(II) can be determined immediately after the separation of iron(III) by the flame atomic absorption spectrometry. As shown in Table 3, the satisfactory results were obtained with the synthesised sample solutions containing both 5-20 μg of iron(II) and 5-15 μg of iron(III).

Determination of Trace Iron(III) in Mohr's Salt

In the proposed method, a large amount of iron(II) also does not interfere with the iron(III) determination when the extraction is carried out in a stream of nitrogen (Table 1). So, the determination of trace iron(III) in Mohr's salt was tried. As shown in Table 4, the results obtained by this method and by Mohr's titration method[23] were in good agreement with each other.

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