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Studies on the Sulfur-containing Chelating Agents. XLIII.[1] The Reaction of Thio-β-diketones and the Related Compounds with Iron(II) in the Presence of Pyridine

Masahiko Chikuma, Akira Yokoyama, Yasuko Ooi, and Hisashi Tanaka

Faculty of Pharmaceutical Sciences, Kyoto University[2]

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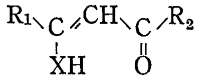
The formations of the adduct complex of the type (ligand)$_2$ Fe(II) (base)n ($n=1$ or 2) were observed in the reacton of some thio-β-diketones, and the corresponding β-diketones with iron(II) ion in the presence of pyridine base. Paramagnetic shifts were observed in γ-picoline adducts. The use of thiothenoyltrifluoroacetone, thiodibenzoylmethane and dibenzoylmethane gave satisfactory result in the determination of less than 60 μg of iron as an extraction-spectrophotometric reagent, based on their adduct formation reaction with pyridine.

The metal complex formation of thio-β-diketones and the related amides and esters has been studied extensively in recent years.[3] In a previous paper,[4] the determination of the stability constants of some metal chelates of thiodibenzoylmethane and N-phenyl- and N-ethyl-β-mercaptocinnamamides by solvent extraction method was reported. The reaction of the chelating agents containing thiol group with metal ion whose valency is variable are expected to be complicated on account of the occurrence of the redox reaction in parallel with the chelate formation. In addition, studies on the coordination between sulfur and iron which shows sometimes high affinity to sulfur may be of some interest in connection with the softness of iron. The present paper deals with the reaction of thio-β-diketones and the related amides and esters with iron(II) in the presence of pyridine base. It was observed that iron(II) reacts with thiothenoyltrifluoroacetone (STTA) and thiodibenzoylmethane (SBB) to form green adduct complexes which can be quantitatively extracted in benzene, and a method of the determination of iron with STTA and SBB as the extracting and colorimetric reagent may be proposed. The reaction of iron(II) with β-diketones and related amides and esters as the oxygen analogues was also investigated. The reagents used in the study are shown in Chart 1, together with their abbreviations.



$$\underset{\text{XH}}{\overset{R_1}{\diagdown}C}{=}CH-\underset{\text{O}}{\overset{}{C}}(=O)\text{-}R_2$$

R_1	R_2	X=S	X=O
2-C_4H_3S	CF_3	thiothenoyltrifluoroacetone (STTA)	thenoyltrifluoroacetone (TTA)
C_6H_5	C_6H_5	thiodibenzoylmethane (SBB)	dibenzoylmethane (BB)
C_6H_5	NHC_6H_5	N-phenyl-β-mercaptocinnamamide (PMC) (thiobenzoylacetanilide)	N-phenyl-β-hydroxycinnamamide (PHC) (benzoylacetanilide)
C_6H_5	OC_2H_5	ethyl thiobenzoylacetate (SEBA)	ethyl benzoylacetate (EBA)

Chart 1

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[1] Part XLII: M. Chikuma, A. Yokoyama, Y. Ueda, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 23, 473 (1975).

[2] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*

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Experimental

Materials——STTA,[5] SBB,[6] PMC,[7] and SEBA[8] were prepared and purified by the method reported previously. TTA, BB, PHC, and EBA were obtained from the Dojindo Co., Ltd. and the Tokyo Kasei Kogyo Co., Ltd. Pyridine, α-, β-, and γ-picoline were dried over KOH and constant boiling fraction was collected before use. Benzene was distilled over Linde 4A molecular sieves. All the other reagents used were commercially available reagent grade materials. The stock solution of iron(II) was prepared by dissolving the requisite amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 1000 ml of distilled water containing 3 ml of concentrated sulfuric acid. The buffer solution was prepared by 0.1 M HCl, 0.1 M HOAc and 0.1 M NaOAc. The solution of 0.1 M hydroxylamine hydrochloride (0.5 ml) was added before the reagent was added in the case of TTA, BB, PHC, and EBA.

Apparatus and Procedure——The pH value of about 10 ml of the aqueous solution which contains iron(II) or iron(III) ion was adjusted to a desired value, and the solution was shaken mechanically with 6 ml of benzene which contains the ligand and pyridine in a thermostated room at 22±1° until the extraction equilibrium was reached. After centrifugation, the electronic spectrum and the optical absorption of the organic phase were measured with a Shimadzu spectrophotometer Model D-40 and QV-50 respectively. The pH value of equilibrated aqueous phase was measured by a Hitachi Horiba F-5 type pH meter.

Nuclear magnetic resonance (NMR) spectra were measured at 60 Mc with a Varian A-60 NMR spectrometer by the use of TMS as an internal standard at room temperature. The mixture of 1 ml of 0.005 M iron(II) solution, 3 ml of 0.5 M NaOAc solution, 1.5 ml of 0.1 M ligand deuterochloroform solution and 0.2 ml of γ-picoline was shaken for one minute and centrifuged, 0.5 ml aliquot of the organic phase was taken for NMR measurement.

Results and Discussion

In general, β-diketones react with iron(III) ion to form red iron(III) chelates, and the reaction with iron(II) can not be studied in detail because of the autoxidation.[9] Emmert, *et al.*[10] reported that the pyridine adduct complexes of iron(II) chelates of β-diketones such as acetylacetone, benzoylacetone and dibenzoylmethane can be prepared. TTA-iron(II)-pyridine[11] system has been applied to a colorimetric determination of iron(II), based on the characteristic color of the adduct complex. In the case of thio-β-diketones, iron(II) complex can not be prepared easily[12] except for a few cases, namely iron(II) bis(thiodipivaloylmethanato)[13] and iron(II) bis(thiodibenzoylmethanato)dipyridine.[14] We also failed in preparation of iron(II) chelate of other thio-β-diketones and the related compounds used in this study even in nitrogen stream. However, it was observed that iron(II) ion reacts in the presence of pyridine base with STTA or SBB to form stable complex in atmosphere.

The electronic spectra of the extracts of reagent-iron(II)-pyridine system are shown in Fig. 1 and 2. In the cases of TTA and BB systems, the absorption maxima around 580 nm were respectively observed with two shoulders at about 540 and 700 nm. In PHC system, the extracted reddish complex shows a spectrum with an absorption maximum at 489 nm, as previously reported on the iron(III) chelate by Sarkar, *et al.*[15] In EBA system, the spectrum of the complex extracted into benzene shows three discernible shoulders at around 430, 485 and 530 nm as shown in Fig. 3. The spectrum changes with time and finally shows an absorp-

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ption maximum at 455 nm, which is consistent with that of the iron(III) complex. This result suggests that the pyridine adduct of EBA-iron(II) chelate is unstable and converted into iron(III) chelate gradually in organic phase, by air oxidation.

In STTA and SBB systems, the bright green complexes were extracted into benzene which show the absorption spectra of the similar shape but with the absorption maxima observed at longer wavelength region than those of the oxygen analogues, TTA and BB. In PMC system, also a green complex is extracted into benzene but precipitated in benzene when the concentration of pyridine was below 0.1 M. The shape of the absorption spectrum is different from that of STTA or SBB. Even in the presence of pyridine, adduct complex was not formed in the reaction of PMC with iron(II) ion but iron(III) chelate was formed, which was confirmed by the elemental analysis and the molar-ratio determination by the continuous variation method in the presence of pyridine.[16] In SEBA system, the spectrum of the extract shows an absorption maximum at 700 nm and two shoulders at around 430 and 530 nm. The absorption maximum is consistent with that of the iron(III) chelate of SEBA[17] and the shoulders are considered to be based on the above mentioned pyridine adduct and/or iron(III) chelate of EBA. SEBA reacts with iron(III) in the absence of pyridine to form the blue complex with the absorption maximum at 700 nm without any other band in the visible region. These facts suggest that the thiol group of SEBA is partially hydrolyzed to form EBA in the presence of pyridine.

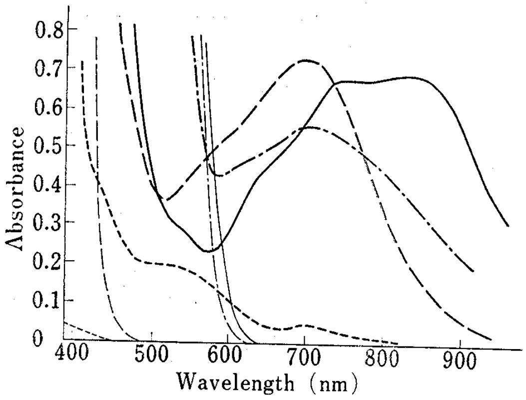

Fig. 1. Absorption Spectra of Extracts in Thio-β-diketones and the Related Compounds -Fe (II)–Pyridine Systems

STTA system contains 0.005 M STTA and 1.6 M pyridine.
Other system contains 0.01 M reagent and 2.0 M pyridine.
Fe(II) ion: 55.9 μg, benzene: 6 ml,
——: STTA, - - -: SBB, —·—: PMC, ------: SEBA
reagent blank (0.01 M): ——: STTA, - - -: SBB, ——: PMC, ------: SEBA

The compositions of the adduct complexes were determined by the use of molar ratio method for STTA system and continuous variation method for SBB and BB systems as shown in Fig. 4 and 5. In these three adduct complexes the ratios of reagent to iron were always found to be 2. The determination of the composition of the pyridine adduct of EBA-iron(II) chelate with the continuous variation method was unsuccessful because of the considerably low stability of the mother iron(II) chelate and/or the iron(III) chelate formed by air oxidation.

The NMR spectra of the extracts in STTA, SBB, TTA, BB, and EBA-iron(II)-γ-picoline systems are shown in Fig. 6. The signals of the α- and β-protons of γ-picoline are remarkably broadened and shifted to lower fields in the presence of iron(II), while the γ-methyl signal also is broadened and shifts to upper field. The present results, which show the paramagnetic shift based on d^6 iron(II) ion, suggest that unpaired spin density transfers directly to γ-picoline *via* the σ-bonding framework and gives positive spin density at α-CH and β-CH of γ-picoline. Positive methyl proton shifts observed suggest that unpaired spin density is introduced into π orbitals via an indirect mechanism as well as in the γ-picoline adducts of bis(acetylacetonato)-nickel(II) and cobalt(II).[18] These paramagnetic shifts of γ-picoline in EBA system was much smaller than those of the other systems under the same condition because iron ion was not completely extracted into benzene. In ten fold concentration of the reagent, the paramagnetic shifts of similar extent to those of the other systems were observed as shown in Fig. 6.

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[16] M. Chikuma, A. Yokoyama, Y. Ooi, and H. Tanaka, unpublished.
[17] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (Tokyo), **10**, 19 (1962).
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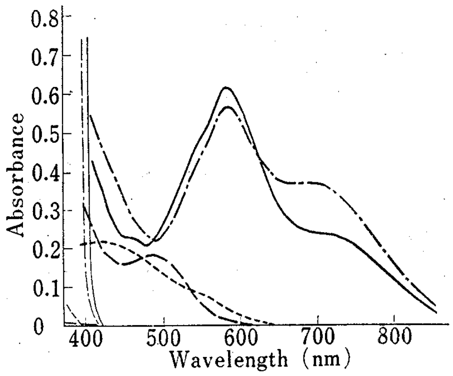

Fig. 2. Absorption Spectra of Extracts in β-Diketones and the Related Compounds -Fe(II)–Pyridine Systems

reagent: 0.01M, pyridine: 2M
Fe(II) ion: 55.9 μg, benzene: 6 ml
——: TTA, – – –: BB, — —: PHC,
········: EBA
reagent blank (0.01M): ——: TTA, – – –:
BB, ——: PHC, – – –: EBA

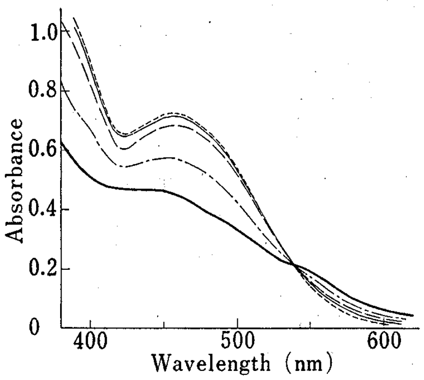

Fig. 3. Effect of Time on Absorption Spectra of Extract in EBA System

EBA 0.5M EtOH soln.	1 ml
pyridine	1 ml
Fe^{2+} (or Fe^{3+}) 0.001M	1 ml
buffer (pH 6.50)	5 ml
benzene	5 ml

——: immediately after extraction
——: after 24 hr — —: after 48 hr
——: after 72 hr – – –: Fe(III) ion was used.

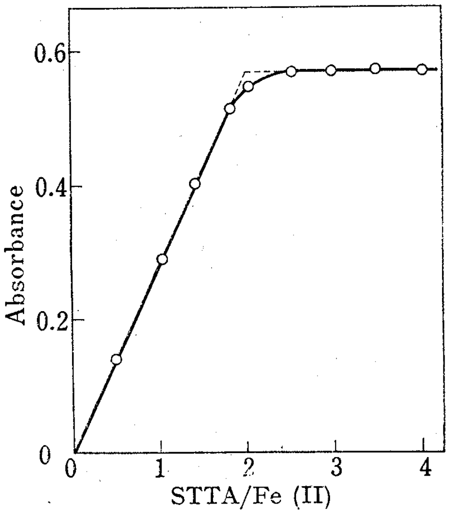

Fig. 4. Determination of Composition of Pyridine Adduct of Fe (II) -STTA Chelate

Fe(II) ion: 8.3×10^{-4} mole, pyridine: 0.8 ml
benzene: 5 ml, pH 6.99

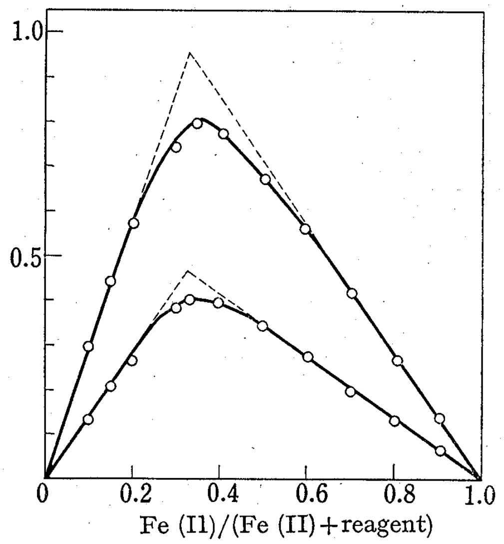

Fig. 5. Determination of Composition of Pyridine Adducts Complex

○: SBB, total amount of Fe(II) ion and SBB: 5×10^{-5} mole, pyridine: 1 ml, benzene: 5 ml, pH 6.97, 1 mm cell
●: BB, total amount of Fe(II) ion and BB: 5×10^{-6} mole, pyridine: 1 ml, benzene: 5 ml, pH 6.95, 10 mm cell

This result suggests the low stability of the pyridine adduct of EBA-iron(II) chelate. In conclusion, iron(II) ion reacts with thio-β-diketones, β-diketones and β-ketoester used in this study in the presence of pyridine base to form the adduct of $(\text{reagent})_2\text{iron(II)}(\text{Py})_n$ ($n=1$ or 2). The value of n was reported to be 2 on the basis of elemental analysis for BB[10b] and SBB,[14] and solvent extraction method for TTA[11] systems.

When some nitrogen bases instead of pyridine were added in STTA and BB systems, the positions of the band observed at the lowest wave-number were linearly correlated with the pK_a values of the bases used both in STTA and BB systems as shown in Fig. 7. The absorption bands were observed at lower wave-number as the pK_a value of the base increased.

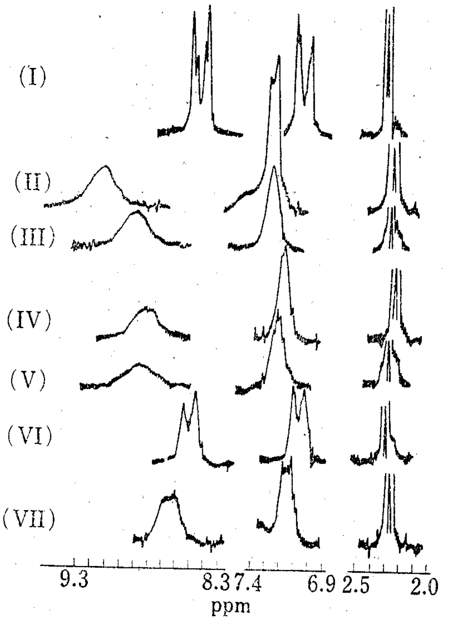

Fig. 6. PMR Spectra of γ-Picoline in Extracts of Fe(II)-γ-picoline-reagent System

(I): γ-picoline in the absence of reagent
(II) SBB, (III) STTA, (IV) BB, (V) TTA,
(VI) EBA:

reagent 0.1M $CDCl_3$ soln.	1.5 ml
γ-picoline	0.2 ml
NaOAc 0.5M aq. soln.	3.0 ml
Fe^{2+} 5×10^{-3}M	1.0 ml

(VII) EBA: reagent 1.0M $CDCl_3$ soln.

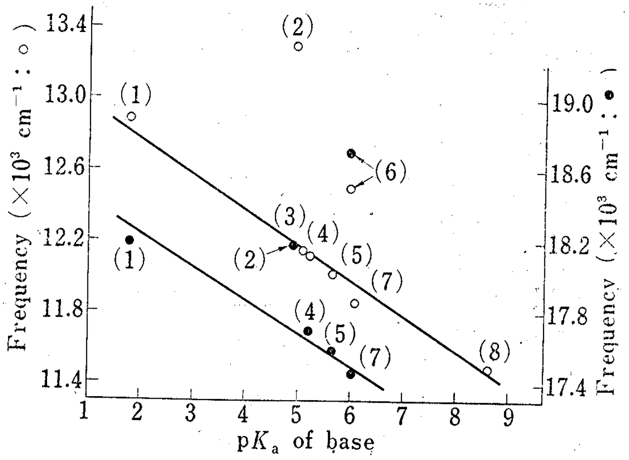

Fig. 7. Relationship between Basicity of Nitrogen Base and Frequency of Absorption Maximum of the Base Adduct of Fe (II) Chelate

○: STTA, ●: BB
(1) 4-cyanopridine, (2) quinoline, (3) isoquinoline, (4) pyridine, (5) β-picoline, (6) α-picoline, (7) γ-picoline, (8) morpholine

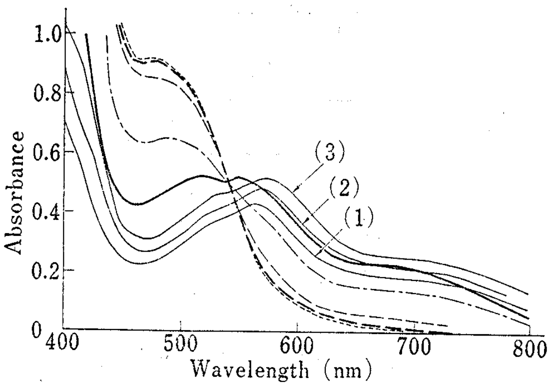

Fig. 8. Absorption Spectra of Base Adduct of Fe (II) Chelate of BB in Aqueous EtOH Solution

——: (1) pyridine, (2) β-picoline, (3) γ-picoline;
——: α-picoline immediately after reaction,
–·–·–: α-picoline (after 3 min),
– – –: α-picoline (after 10 min)
— —: α-picoline (after 20 min)
------: pyridine, Fe^{3+} ion

BB: 0.01M EtOH soln. 2.5 ml
Fe^{2+} (or Fe^{3+}): 0.001M aq. soln. 1 ml
base: 1 ml

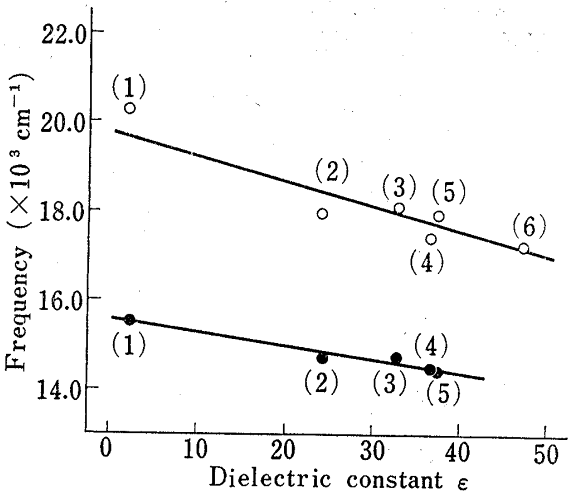

Fig. 9. Relationship between Dielectric Constant of Solvent and Frequency of Absorption Maximum

○: BB ●: SBB
reagent 0.01M soln. 4 ml
pyridine 0.5 ml
Fe^{2+} 0.002M aq. soln. 0.5 ml
(1) dioxane, (2) EtOH, (3) MeOH, (4) dimethylformamide, (5) acetonitrile (6) dimethylsulfoxide.

The values of dielectric constant of dimethylsulfoxide and the other solvents are cited from the following references, respectively:
R.A. Hovermale and P.G. Sears, *J. Phys. Chem.*, **60**, 1579 (1956). J.A. Riddick and E.E. Toops, Jr., "Organic Solvents," 2nd ed., by A. Weissberger, Interscience Publishers, Inc., New York, N.Y., 1955.

Considerable deviations obsreved in α-picoline and quinoline may be explained from the steric hindrances of methyl group and benzene ring. In fact, a remarkable effect of steric hindrance on the stability of adduct was observed in BB-iron(II)-α-picoline system. The spectra of BB-iron(II)-pyridine bases systems in aqueous ethanol solution are shown in Fig. 8. In the cases of pyridine, β- and γ-picoline, the absorbances are almost constant for at least 3 hr but in α-picoline the spectrum changes with time with an isosbestic point (540 nm) and becomes stable after 20 min, to form a red colored complex. The visible absorption spectrum of the red complex is similar to that of the iron(III)-BB chelate. This spectral change does not occur in a stream of nitrogen. These results suggest that the ability of the adduct formation may be weaker in α-picoline than other bases on account of the steric hindrance. The formation of iron(III) chelate in the presence of α-picoline may be explained from the lability of the adduct complex, provided that oxygen and pyridine base compete in the oxidation of the complex as previously reported.[19]

The results of the measurements of the absorption spectra of the pyridine adduct complexes of SBB and BB in some solvents which are miscible with water are shown in Fig. 9. In more polar solvent, the absorption maxima were observed in a little lower energy region. This result suggests that these bands are regarded to be charge transfer of some kind as discussed on the spectra of (dioxime)$_2$iron(II)(pyridine)$_2$ by Sanders, *et al.*[20]

The iron complexes extracted with the reagents used in this study into benzene in the absence or the presence of pyridine were summarized in Table I. The pyridine adduct complex formations were not confirmed in the amides because their adduct complexes are not stable enough to resist against air oxidation. We reported in a previous paper[19] that both SBB and PMC react with nickel(II) or cobalt(II) in the presence of pyridine base to form their pyridine adduct complexes. With iron(II) ion, however, SBB and PMC react in the presence of pyridine to form the pyridine adduct of iron(II) chelate and the iron(III) chelate respectively.

The results of the reaction with iron(III) ion were included in Table I for comparison. STTA-iron(III)-pyridine system is regarded as the only case where iron(III) ion was reduced

TABLE I. Valency of Iron Complex Extracted and Extraction Rate

Reagent[a]	No Base		Pyridine	
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
SBB	Fe(III)[b]	Fe(III)[b]	Fe(II)[c] fast	Fe(III)[b]
STTA	Fe(III)[b]	Fe(III)[b]	Fe(II)[c] fast	Fe(II)[b,c,d]
PMC	Fe(III) fast	Fe(III) fast	Fe(III) fast	Fe(III) fast
SEBA	Fe(III)[b]	Fe(III)[b]	Fe(III)[b,e]	Fe(III)[b,e]
BB	Fe(III)[b]	Fe(III)[b]	Fe(II)[c] fast	Fe(III)[b]
TTA	Fe(III)[b]	Fe(III)[b]	Fe(II)[c] fast	Fe(III)[b]
PHC	Fe(III)[b]	Fe(III)[b]	Fe(III)[b]	Fe(III)[b]
EBA	Fe(III)[b]	Fe(III)[b]	Fe(II)[c] fast	Fe(III)[b]

[a] 10^{-2} M benzene soln. iron: 55.9 μg
[b] Extraction equilibrium was not reached within 30 min.
[c] pyridine adduct
[d] Iron was not completely extracted
[e] partially hydrolyzed to EBA

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[19] M. Chikuma, A. Yokoyama, and H. Tanaka, *J. Inorg. Nucl. Chem.*, 37, 199 (1975).
[20] N. Sanders and P. Day, *J. Chem. Soc.* (*A*), **1969**, 2303.

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TABLE II. The Optimum Condition for Determination of Iron(II)

Reagent	pH	Reag. conc. (M)	Py conc. (M)	Time (min)	Sensitivity (μg/cm^2)
SBB	5—7	0.004	1.6	30	0.017(710 nm)
STTA	5—7	0.0004	0.1	3	0.014(826 nm)
BB	6.5—7	0.004	0.4	45	0.018(582 nm)

These results were obtained for the extraction of 55.9 μg of iron(II) into 6 ml of benzene.

TABLE III. Effect of Diverse Ions in SBB System[a)]

Diverse ion	Added as	Diverse ion added (mg)	Absorbance	Fe found (μg)
none	—	—	0.512	50.0
Ca^{2+}	$Ca(NO_3)_2 \cdot 2H_2O$	0.50	0.512	50.0
Sr^{2+}	$SrCl_2 \cdot 6H_2O$	0.50	0.512	50.0
Zn^{2+}	$Zn(OAc)_2 \cdot 2H_2O$	0.50	0.506	49.4
Cd^{2+}	$Cd(OAc) \cdot 2H_2O$	0.50	0.477	46.6
Hg^{2+}	$Hg(OAc)$	0.50	0.481	47.0
Al^{3+}	$AlCl_3$	0.50	0.512	50.0
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	0.50	0.659	64.4
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	0.25	0.512	50.0
		0.50	0.569	55.6
Co^{2+}	$CoCl_2 \cdot 6H_2O$	0.25	0.679	66.3
Ni^{2+}	$Ni(OAc) \cdot 4H_2O$	0.25	0.648	63.3
Cu^{2+}	$CuCl_2 \cdot 2H_2O$	0.40	0.827	80.8
Cl^-	NaCl	50.0	0.509	49.7
SO_4^{2-}	K_2SO_4	50.0	0.516	50.4
tartrate^{2-}	Sodium tartrate	30.0	0.440	43.0
citrate^{3-}	Ammonium citrate	30.0	0.370	36.1
SCN^-	KSCN	30.0	0.515	50.3

a) Fe^{2+}: 50 μg
reagent: 10^{-2}M
pyridine: 2.0M

partially to form the green, pyridine adduct of iron(II) chelate, from the similarity between Fig. 1 and 10. This reaction is slow and not quantitative under the condition studied. Other reagents, regardless of the presence of the thiol group, react with iron(III) ion to form their brown or red iron(III) chelates in the presence of pyridine as in the absence of pyridine. In SBB-iron(III)-pyridine system, the iron(III) chelate is formed and extracted into benzene, but the reaction is so slow that no iron(III) ion can be extracted within at least 2 hr, when the concentration is below 250 μg.

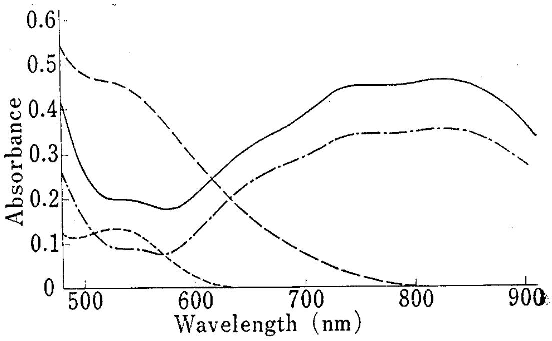

Fig. 10. Absorption Spectra of Extracts in STTA Systems

STTA: 0.0012M benzene phase: 6 ml
———: pyridine 1.6M, Fe(III) ion 250 μg, pH 6.74
— —: pyridine none, Fe(III) ion 250 μg, pH 4.91
------: pyridine none, Fe(II) ion 55.9 μg, pH 3.82
—·—: pyridine 1.6M, Fe(II) ion 28.0 μg, pH 5.48

Direct determinations of iron using STTA, SBB and BB are possible by the measurement of the absorbancies of the charge transfer bands, of their adduct complexes because the reagents do not exhibit any unfavorable absorbance at the wavelength of the absorption maxima of the adducts as shown in Fig. 1 and 2.

The optimum conditions are summarized in Table II. The optimum range of pH was determined above 5.0 because the pK_a value of pyridine is reported to be 5.18.[21] Sensitivities are indicated according to Sandells' definition.[22] The addition of reducing agent is necessary in the use of TTA and BB, but satisfactory result was obtained without reducing agent in the use of STTA and SBB. The effect of diverse ions on the absorbance of the pyridine adduct complex of SBB was examined as shown in Table III. The results obtained in STTA system were almost similar to SBB system. The effect of the diverse ions in BB system was almost similar to TTA system.[11] When 0.1 M hydroxylamine hydrochloride solution is added before reagent is added under the condition shown in Table II, iron(III) ion also can be extracted quantitatively as pyridine adduct of iron(II) chelate. These three reagents, STTA, SBB and BB are considered to be useful as analytical reagent for the determination of iron, although the sensitivities of method by these reagents are slightly lower than that of *o*-phenanthroline method.[22]

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21) L.G. Sillèn and A.E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

22) E.B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed., Interscience Publishers, Inc., New York, N. Y., 1959.