Selective Extraction Spectrophotometric Determination of Iron by Utilizing the Peculiar Absorption of Iron(II)-2-(2-Thiazolylazo)-5-dimethylaminophenol Complex

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Thiazolylazo compounds react with iron(II) to form brownish complexes, which show a characteristic absorption in near-infrared region. These compounds possess the hydroxyl group in the *o*-position next to the azo group. Among them, iron(II)–2-(2-thiazolylazo)-5-dimethylaminophenol complex has the absorption maximum at 760 nm in chloroform; the optimum pH for iron extraction lies between 8.2—10.0. Beer's law holds up to 2.0 μg cm^{-3} of iron and the molar absorption coefficient is 2.70×10^4 dm^3 mol^{-1} cm^{-1}. The composition and the extraction constant of the complex are estimated to be Fe: TAM=1 : 2 and log $K_{ex}=-4.20\pm0.04$, respectively. Since the present method utilizes the specific absorption of the iron(II)–TAM complex, the presence of many ions is tolerable, especially of 3d type metals. The method was applied to the determination of traces of iron dissolved in river and sea waters with satisfactory results.

Many azo compounds containing a hetero ring are useful as analytical reagents.[1,2] Above all, thiazolylazo derivatives are especially attractive, because their complexing properties are often specific.[3,4] In previous papers, the authors reported highly selective spectrophotometric methods for the determination of iron with 4-(2-thiazolylazo)resorcinol[5] and 2-(2-thiazolylazo)-4-methylphenol[6] by utilizing the specific absorption of iron(II) complexes in the near-infrared region. The homolog 2-(2-thiazolylazo)-5-dimethylaminophenol (TAM) has been applied for the determination of specific metals, such as uranium,[7] vanadium,[8] niobium,[9] bismuth,[10] yttrium,[11] nickel,[12] titanium,[13] zirconium,[14] and thorium.[15] We investigated the color reaction of TAM with iron(II) and recognized that iron(II)–TAM complex also showed a characteristic absorption at 760 nm. It is rarely the case that a metal complex possesses the absorption maximum in this infrared region. In this research, the fundamental conditions for the selective extraction spectrophotometric determination of traces of iron were investigated. We also prepared eleven (thiazolylazo)phenol and naphthol derivatives in order to elucidate these absorption features and obtained some information about the substituent effect of the chelate ligand and the nature of iron(II) complex.

Experimental

Reagents. Thiazolylazo compounds were synthesized by the diazotization of 2-aminothiazole (or 2-amino-4-methylthiazole and 2-aminobenzothiazole) with nitrous acid and the subsequent coupling with phenols (or naphthols) at 0 °C.[4,16,17] Phenols used were resorcinol, 4-chlororesorcinol, orcinol, *m*-methoxyphenol, *m*-dimethylaminophenol, *p*-methoxyphenol, *p*-chlorophenol, 2,4-dimethylphenol, and pyrocatechol; naphthols were 2-naphthol and 2-naphthol-3,6-disulfonic acid. The products were purified by repeated crystallization with ethanol or re-precipitation with dilute hydrochloric acid and were identified by elementary analyses. TAR, TAM, TAC, and TAN were commercially available and were used without further purification. The standard iron(II) solution was prepared by dissolving ammonium iron(II) sulfate hexahydrate in deionized distilled water. The solution was acidified to pH 1 by sulfuric acid and was standardized by permanganometry. A 0.05% TAM solution was prepared by dissolving the Dotite TAM in ethanol. A fresh 0.1% ascorbic acid solution was prepared every three days. All the other chemicals used were of guaranteed reagent quality.

Apparatus. A sample solution was prepared in a 50 cm^3 graduated centrifuge tube with a glass-stopper; the solution was shaken in an Iwaki-KM type reciprocating shaker. A Kubota K-80 type centrifuge with 5000 min^{-1}. was used for phase separation. A Hitachi-Horiba model M-5 pH meter equipped with a combined glass electrode was used for pH measurements. Absorption spectra and absorbance were measured with a Hitachi 124 recording spectrophotometer and a Hitachi-Perkin Elmer 139 spectrophotometer using 10-mm quartz cells.

Standard Procedure. Transfer the sample solution containing up to 20 μg of iron into a centrifuge tube. Add 1 cm^3 of 0.1% ascorbic acid and 2 cm^3 of 0.05% TAM solutions, and adjust the pH to 9.0 with 5 cm^3 of 1 mol dm^{-3} ammonia buffer solution. Dilute the solution to 20 cm^3 and shake it with 10 cm^3 of chloroform for 5 min. After centrifugal separation, transfer the extract into an absorption cell, and measure the absorbance at 760 nm against the reagent blank.

Results and Discussion

Complexing Properties of Thiazolylazo Compounds with Iron(II). Table 1 shows the complexing properties of (thiazolylazo)phenols and naphthols with iron(II). Thiazolylazo compounds react with iron(II) to form brownish complexes from the weakly acidic to the alkaline region, which have the characteristic absorption maxima beyond 700 nm. The compounds have the phenolic hydroxyl group in the *o*-position next to the azo group; TAPC, possessing this group in the *m*- and *p*-position, shows different absorption features. The bathochromic shift of these absorption maxima is promoted by the resonance effect of the substituent group in the *p*-position to the *o*-hydroxyl group for phenols and of the naphthalene ring for naphthols. TAR, TARCl, and TAM show higher molar absorptivities than TAC, TAMP, and TACl. The difference would come from the inductive and the resonance effects of the substituent in the *m*- and *p*-position to the *o*-hydroxyl group. The derivatives possessing resorcinol

Table 1. Complexing properties of thiazolylazo compounds with iron(II)

Systematic name (abbreviation)	λ_{max} / nm	ε / $dm^3\ mol^{-1}\ cm^{-1}$	pH	Solvent
4-(2-Thiazolylazo)resorcinol (TAR)[5]	730	2.90×10^4	8.9—10.3	Water
4-(2-Thiazolylazo)-6-chlororesorcinol (TARCl)	740	2.90×10^4	9.2—10.5	Water
4-(4-Methyl-2-thiazolylazo)resorcinol (MeTAR)	737	2.45×10^4	9.0—10.0	Water
4-(2-Thiazolylazo)orcinol (TAO)	742	2.02×10^4	9.0	Water
2-(2-Thiazolylazo)-5-methoxyphenol (TAMR)	720	1.59×10^4	8.0— 9.0	Water
2-(2-Thiazolylazo)-5-dimethylaminophenol (TAM)	760	2.70×10^4	8.2—10.0	Chloroform
2-(4-Methyl-2-thiazolylazo)-5-dimethylaminophenol (MeTAM)	765	2.71×10^4	5.5— 9.0	Chloroform
2-(2-Thiazolylazo)-4-methylphenol (TAC)[6]	762	1.37×10^4	4.8—10.2	Chloroform
2-(2-Thiazolylazo)-4-methoxyphenol (TAMP)	784	1.57×10^4	5.0— 9.0	Chloroform
2-(2-Thiazolylazo)-4-chlorophenol (TACl)	757	1.36×10^4	5.8— 8.5	Chloroform
2-(2-Thiazolylazo)-4,6-dimethylphenol (TACMe)	762	9.38×10^3	5.5— 7.5	Chloroform
4-(2-Thiazolylazo)pyrocatechol (TAPC)	590	3.43×10^4	6.5	Water
1-(2-Thiazolylazo)-2-naphthol (TAN)	786	1.89×10^4	3.5—10.0	Chloroform
1-(4-Methyl-2-thiazolylazo)-2-naphthol (MeTAN)	790	4.03×10^3	5.0—10.0	Chloroform
1-(2-Thiazolylazo)-2-naphthol-6-sulfonic acid (TAN6S)	761	4.19×10^3	4.8— 8.5	Water

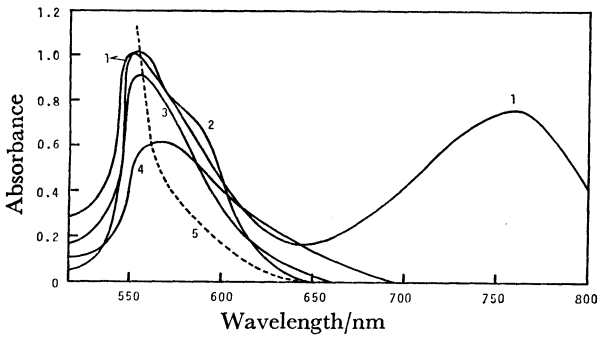

Fig. 1. Absorption spectra of TAM complexes.
pH: 9.0, 0.05% TAM: 2 cm^3, 0.1% ascorbic acid: 1 cm^3. 1: Fe (15 μg), 2: Ni (10 μg), 3: Cu (10 μg), 4: Co (10 μg), 5: reagent blank.

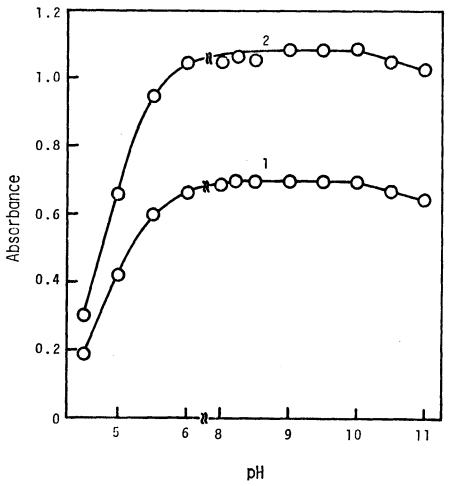

Fig. 2. Effect of pH.
Fe: 15 μg, 0.05% TAM: 2 cm^3, 0.1% ascorbic acid: 1 cm^3. 1: 760 nm, 2: 550 nm.

ring show higher molar absorptivities, but naphthols give lower ones. The effect of the substituent group in the thiazole ring is not so noticeable.

Absorption Spectra. The iron(II) complexes of thiazolylazo compounds usually have two or three absorption maxima. Fig. 1 shows the absorption spectra of 3d type metal–TAM complexes extracted into chloroform. The iron(II) complex has two maxima at 550 nm and 760 nm, while the other 3d type metal complexes have only one maximum near 550 nm. We could not observe any other metal–TAM complex which showed an absorption maximum over 700 nm, hence this maximum at 760 nm is thought to be the characteristic absorption for iron(II). It is not an easy matter to assign these characteristic absorption bands clearly. The configuration of iron(II) complex may differ from those of the other 3d type metal complexes, or thiazole sulfur atom might follow the peculiar behavior on the complexation. But there is some evidence that TAN forms an octahedrally configurated inner complex with iron(II),[18] which is just the same as those of $[Ni^{II}(TAN)_2]$,[19] $[Zn^{II}(TAN)_2]$, and $[Co^{III}(TAN)_2]^+$,[20] and thiazole sulfur atoms never participate in the coordination. The iron(II)–TAN complex also shows the specific absorption at 786 nm in chloroform. Even if iron(II)–TAM complex would take the same configuration as those of the other 3d type metal complexes, its characteristic absorption is thought to be caused by the $t_{2g}\rightarrow\pi^*$ transition of the iron's 3d electrons.[21] As the TAM blank shows no absorption above 650 nm, one might expect the enhancement of the accuracy for the determination of iron.

Effect of pH. The effect of pH on the extraction of iron(II)–TAM complex was examined, as shown in Fig. 2. The extract shows a constant absorbance over the pH range from 8.2 to 10.0. A decrease of the absorbance in the acidic region is attributable to the incomplete formation of the iron(II)–TAM complex, owing to the protonation of the thiazole nitrogen atom.[4]

Choice of Buffering Agent. The iron complex is stable even in relatively higher concentration of ammonia solution, and a constant absorbance is obtained by adding from 2 to 10 cm^3 of 1 mol dm^{-3} ammonia buffer solution. The use of diethylbarbiturate and borax buffer reduces the absorbance, moreover, reproducible absorbances were not obtained. Taking into account the masking effect, 5 cm^3 of 1 mol dm^{-3} ammonia buffer solution was used.

Effect of TAM Concentration. A constant absorbance was obtained by adding from 0.4 to 5.0 cm³ of 0.05% TAM solution for 15 μg of iron. Though 2 cm³ of 0.05% TAM solution was used in practice, the amount corresponds 14.5 times excess to that of iron, calculating in molar ratio. If the consumption of TAM is noticeable owing to the coexistence of other metal ions in some sample, further addition of TAM may be allowed, because the absorbance of the reagent blank is negligible.

Effect of Reducing Agent. The iron(III)–TAM complex shows a weak color ($\varepsilon=1.30\times10^3$ at 760 nm); the rate of complexation reaction is slow. But the reaction of iron(II) with TAM is completed almost in a moment, so it is necessary to fix the oxidation number of iron to iron(II). The effect of addition of ascorbic acid and hydroxylamine hydrochloride was examined, but no significant differences were found. In this work, ascorbic acid was used and a constant absorbance was obtained by adding from 1 to 10 cm³ of 0.1% ascorbic acid. As ascorbic acid forms a 2 : 1 complex with iron(II),[22] it may act as an assistant chelating agent as well as a reducing agent.

Organic Solvent. The chelate was effectively extracted into such hydrocarbons as carbon disulfide ($\varepsilon=2.75\times10^4$, 779 nm), dichloromethane, 1,2-dichloroethane, trichloroethylene, and aromatic hydrocarbons such as benzene (2.72×10^4, 769 nm), toluene, xylene (2.37×10^4, 769 nm), and chlorobenzene. The other ketones and esters show low absorbance, as compared with chloroform, and MIBK destroys the chelate during the extraction. Chloroform was used in practice, because of its fine phase separation and ease of use.

Composition of Iron(II)–TAM Complex. The result obtained by the continuous variation method is shown in Fig. 3; from this it can be confirmed that iron(II) forms a 1 : 2 complex with TAM. As thiazolylazo derivatives generally act as tridentate ligands,[23] this complex will be an inner complex of the six-coordinate octahedral type,[18] and supplementary ligands such as hydroxyl group, ascorbic acid and ammonia would not participate in the complex system.

Extraction Equilibrium of Iron(II)–TAM Complex. When $pK_2(8.65)>pH>pK_1(3.13)$,[24] most of the TAM is present in chloroform, and the iron(II) complex formed is also readily extracted into the organic phase. If auxiliary ligands would not participate in the chelate, the following extraction equilibrium can be considered:

$$M + 2HR_{(o)} \rightleftarrows MR_{2(o)} 2H^+, \quad K_{ex} = \frac{[MR_2]_o[H^+]^2}{[M][HR]_o^2}, \quad (1)$$

where M, R, and K_{ex} denote the iron ion, TAM, and the extraction constant, respectively, and the subscript o refers to the organic phase. From Eqs. 1 and 2 can be derived:

$$\log K'_{ex} = \log \frac{[MR_2]_o}{[M][HR]_o^2} = \log K_{ex} + 2pH. \quad (2)$$

The value of $\log K'_{ex}$ can be calculated by the measurement of the absorbance. The results are shown in Fig. 4. The plots of $\log K'_{ex}$ against pH show a good linearity, and the slope is 2.0, which indicates that Eqs. 1 and 2 are reasonable. The calculated value of $\log K_{ex}$ is -4.20 ± 0.04. The extractabilities of 3d type metal complexes of TAM were also examined, and the order of the half extraction pH was Cu(4.8)<Ni(5.3)<Fe(5.5)<Co(6.4)<Zn(7.5). Nickel, cobalt, and zinc complexes showed smaller slopes than iron's. These facts indicate that auxiliary ligands may participate in the chelate systems or the rates of the complexation with TAM are slow except iron.

Calibration Curve. A calibration curve was made under the optimum conditions. The curve obeys Beer's law up to 20 μg of iron per 10 cm³ of chloroform. The optimum concentration range for the accurate determination of iron evaluated by Ringbom's method[25] is 0.3 to 1.2 ppm of iron, corresponding to absorbance values of 0.2 to 0.8 unit. The molar absorption coefficient and Sandell's sensitivity index for $\log I_0/I=0.001$ are 2.70×10^4 dm³ mol⁻¹ cm⁻¹ and 2.07×10^{-3}

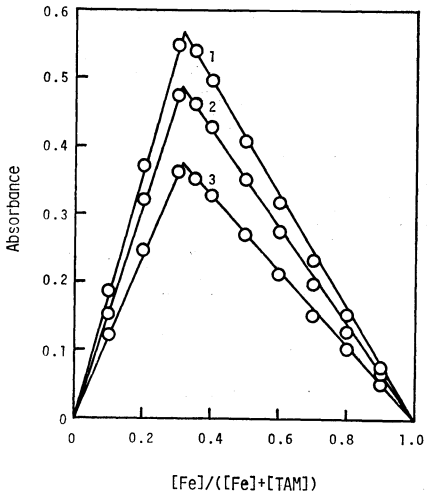

Fig. 3. Continuous variation method.
[Fe]+[TAM]=7.892×10^{-5} mol dm⁻³, pH: 9.0. 1: 760 nm, 2: 740 nm, 3: 720 nm.

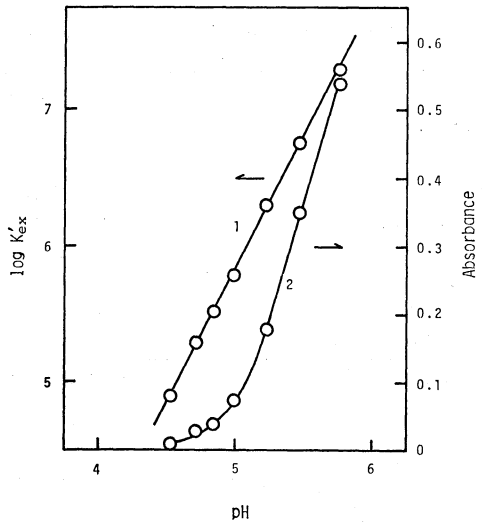

Fig. 4. The plots of $\log K'_{ex}$ and absorbance *vs.* pH at 760 nm.
[Fe]=2.686×10^{-5} mol dm⁻³, [TAM]=4.124×10^{-4} mol dm⁻³, μ=0.1 (KCl). 1: $\log K'_{ex}$ *vs.* pH, 2: absorbance *vs.* pH.

TABLE 2. EFFECT OF CATIONS

Cations added	Tolerance limit(ppm)
Li(I), Na(I), K(I)	30000
As(V), Mo(VI), W(VI), Ca(II)	1000
Mg(II), Sr(II), Ba(II), Cu(II),[a] V(V), Cr(III), Bi(III), Se(IV), Th(IV), Ga(III), Ge(IV), Ag(I)	500
Zn(II), Hg(II), Al(III), Sn(II), Sb(III), Rh(IV), Tl(III)	100
Mn(II), Pd(II), Pb (II), U(VI), Au(III), Ti(IV), Zr(IV), Hf(VI), Ce(III)	50
Ni(II)[b]	30
Cd(II), Co(II),[b] Pt(IV), Ru(III), In(III)	20
Cu(II), Ni(II), Co(II)	8

Iron taken: 1.5 ppm. a) and b): Ten cm^3 of 2% thiosemicarbazide and three cm^3 of 1 % dimethylglyoxime solutions were added, respectively.

TABLE 3. EFFECT OF ANIONS

Anions added	Tolerance limit(ppm)
Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, SCN^-, Acetate	50000
F^-, CO_3^{2-}, Thiosemicarbazide, Thiourea	20000
Tartrate	10000
Oxalate	3000
Dimethylglyoxime	3000
Citrate	1000

Iron taken: 1.5 ppm.

TABLE 4. DETERMINATION OF IRON IN SYNTHETIC SEA WATER

Iron added (μg)	Iron found (μg)	Error (%)
5.00	5.11[a]	2.2
10.00	10.05	0.5
15.00	15.29	1.9
20.00	20.16	0.8

a) The values obtained were averages of 5 determinations.

TABLE 5. DETERMINATION OF IRON IN NATURAL WATER

Sample	Sample volume cm^3	Iron content ppm
Sair iver		
Uchikawa	100	0.026(0.023)[a]
Okuwa	100	0.034(0.035)
Kamikiku	100	0.027(0.024)
Mikage	100	0.025(0.025)
Outfall	100	0.143(0.140)
Kanazawa port	500	0.012(0.015)
Kanaiwa breakwater	500	0.026(0.028)

a) The values obtained by A.A.S. are shown in parentheses.

μg cm^{-2}, respectively, which is more sensitive than the most common reagents,[26] such as 1,10-phenanthroline, 4,7-dihydroxy-1,10-phenanthroline, 2,2′-bipyridine, 2,4,6-tri(2-pyridyl)-1,3,5-triazine, and 1-(2-pyridylazo)-2-naphthol. The variation coefficient of the absorbance for 1.50 ppm of iron is 0.67%; this was determined by ten measurements.

Effect of Diverse Ions. Thiazolylazo dyes generally give similar colored complexes, especially with some of transition metals. That is a disadvantage from the practical viewpoint. As the present method utilizes the specific absorption of iron(II)–TAM complex, the selectivity is significantly elevated. The effect of diverse ions are summarized in Table 2 for cations and in Table 3 for anions, where the tolerance limit is set to ±5% for iron recovery. Iron can be determined in the presence above 20 ppm each of 41 metal ions, where vanadium, bismuth, thorium, uranium, titanium, and zirconium, whose spectrophotometric determinations have already been developed, are tolerable even in large amounts. 3d type metals form colored complexes, but copper can be effectively masked by thiosemicarbazide and nickel, and cobalt by dimethylglyoxime. Since concentrations of these ions in most natural waters are usually low, their interferences are almost negligible. Among the anions tested, acetate, tartrate, thiourea, and citrate can also serve as masking agents.

Determination of Iron in River and Sea Waters. In order to apply the present method to natural waters, we determined iron first in synthetic sea waters.[27] Sea water usually contains 10 ppb order of iron.[28] So known amounts of iron were added to synthetic sea waters as shown in Table 4. The results show that the present method is applicable to sea waters within 3% errors. Table 5 shows the results of determinations in the Sai river from the upper stream to the down stream and in sea waters near river ports. These values agreed well with those obtained by atomic absorption spectrometry. For sea waters, the following procedure is recommended. Take an aliquot of sample solution which is filtered off immediately after sampling. Add 2 cm^3 of concd hydrochloric acid and concentrate the solution to 100 cm^3 on the water bath. Add 1 cm^3 of 0.1% ascorbic acid and 5 cm^3 of 10% sodium acetate solutions, and neutralize by ammonia solution. Transfer the solution into a 200 cm^3 separatory funnel, and determine iron according to the standard procedure. For river waters, filtrates were directly used without preconcentration.

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