# Extraction Kinetics and Spectrophotometric Determination of Iron(II) with 2-(2-Thiazolylazo)-4-methoxyphenol

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2-(2-Thiazolylazo)-4-methoxyphenol (TAMP) forms a brownish 2:1 complex with iron(II) in the presence of ascorbic acid; the complex has a characteristic absorption at 784 nm in chloroform. By utilizing this peculiar absorption, selective spectrophotometric determination of iron has been developed. The optimum pH for iron extraction lies between 5.0–9.3 and Beer's law holds up to 5.0 μg/ml of iron. Many type of ions are tolerable. The method was successfully applied to the determination of iron in river waters. The extraction constant of iron(II) complex was log $K_{ex}$=−2.50±0.12 and the extraction mechanism was kinetically investigated. The complexation rate was first-order with respect to iron(II) and TAMP concentrations and independent of ascorbic acid concentration. From these results, the major extraction rate-determining step was concluded to be a 1:1 complexation reaction between iron(II) and dissociated TAMP. Kinetic data and activation parameters for the first-order reaction were determined and discussed.

**Keywords** 2-(2-Thiazolylazo)-4-methoxyphenol, iron determination, spectrophotometry, extraction kinetics, extraction mechanism

Many azo compounds containing a hetero ring are useful as analytical reagents. Above all, thiazolylazo derivatives are attractive, because their complexing behaviors are often peculiar.[1,2] In previous studies, we synthesized a series of 4-(2-thiazolylazo)resorcinol(TAR) and 1-(2-thiazolylazo)-2-naphthol (TAN) derivatives and investigated the properties of these reagents. Iron(II) complexes in these reagents showed characteristic absorptions in near-infrared region and the molar absorptivities were increased by the inductive effect of the para-substituents to the azo group.[3-5] On these bases, the highly selective and sensitive spectrophotometric methods for determination of iron were proposed in the presence of ascorbic acid, which was very useful as a reducing agent, as seen in the vital functions.

In the present study, the complexation reaction of 2-(2-thiazolylazo)-4-methoxyphenol (TAMP) with iron(II) and the extraction behavior of the complex were investigated in the presence of ascorbic acid to develop the selective determination of trace iron. The extraction equilibria and kinetics were studied in detail to fully understand the mechanism, by using the stirring technique.

## Experimental

*Reagents*

TAMP was synthesized as described previously.[3] A standard iron(II) solution was prepared by dissolving ammonium iron(II) sulfate in 0.05 M sulfuric acid and standardized by the titration with permanganate. The freshly prepared ascorbic acid was used. Chloroform was washed with water and distilled before use. All other reagents were of analytical reagent grade. Distilled deionized water was used throughout.

*Apparatus*

A Shimadzu UV-200 S spectrophotometer and a Hitachi-Horiba M-5 pH meter were used. An Iwaki KM type shaker and a Kubota K-80 centrifuge were also used. Extraction kinetics measurements were performed by the stirring method, which was analogous to that described previously.[6] The stir shaft with a Teflon blender was set on a 500-ml Morton flask, fixing with a pulley, and was rotated through a braid by a motor connected to the volt slider. The rotating number of the shaft was measured by an Asahi hand tachometer. The flask was dipped in a thermostatic bath, so that the systems could be kept at constant temperature (±0.1°C). The iron concentrations were measured with a Nippon Jarrel-Ash AA-8500 atomic absorption spectrometer.

*Procedure*

*Spectrophotometric determination of iron.* Transfer the sample solution containing up to 50 μg of iron into a 50-ml centrifuge tube. Add 2 ml each of 0.1%

ascorbic acid and 0.05% TAMP solutions, successively, and adjust the pH to 5.5 with 5 ml of 0.1 M acetate buffer solution. Dilute the solution to 20 ml with water and shake the mixture with 10 ml of chloroform for 1 min. After centrifuging, transfer the extract into an absorption cell and measure the absorbance at 784 nm against the reagent blank.

*Extraction kinetic measurement.* The kinetic runs were carried out under pseudo first-order conditions, the TAMP concentration in the chloroform phase being in a large excess over iron(II) in the aqueous phase. Each phase was prepared in a 100 ml calibrated flask, where an aqueous solution contains iron(II), ascorbic acid, acetate buffer and potassium chloride to maintain the ionic strength to 0.1, and was immersed in a thermostated bath for 30 min. Then the solution were put into the reaction flask: first the aqueous solution, next the heavier chloroform phase, using a long stem funnel to minimize the phase mixing. The mixture stirred by rotating the pulley. At predetermined intervals, the dispersed sample (*ca.* 10 ml) were taken into a centrifugal tube by purging the vessel with nitrogen gas without disturbing the progress of the reaction. After centrifuging, the metal concentration in the upper aqueous phase was determined by means of AAS. The extraction were carried out in the plateau region, the rotating number ranging from 420 to 450 $min^{-1}$. A further increase of stirring speed had no effect on the rate of extraction.

## Results and Discussion

*Spectral characteristics*

The absorption spectra of 3d type metal(II)-TAMP complexes in chloroform are shown in Fig. 1. The iron(II) complex has three absorption maxima at 554, 644 and 784 nm, while the other complexes have only one maximum near 620 nm. Manganese and zinc did not form colored complexes in the presence of ascorbic acid. The maximum at 784 nm in the near infrared region is separated more than 160 nm from those of the other complexes; hence the maximum is regarded as a characteristic absorption for iron(II). We assigned it to $t_{2g}$–$\pi^*$ transition of the 3d electrons of iron, because the iron(II) complex often shows a charge transfer band of the metal–ligand type with a large bathochromic shift.[7] As the TAMP blank shows no absorption above 630 nm, an increase in the accuracy for determination of iron can be expected.

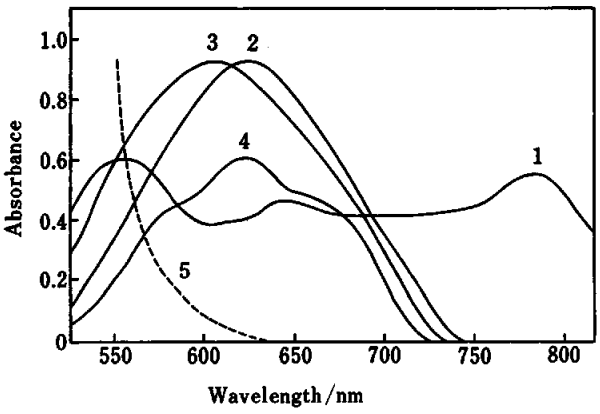


Fig. 1 Absorption spectra of TAMP complexes. pH, 5.5; 0.05% TAMP, 2 ml; 0.1% ascorbic acid, 2 ml. 1, Fe(20 μg); 2, Cu(10 μg); 3, Co(10 μg); 4, Ni(10 μg); 5, TAMP.

*Effect of pH and TAMP concentration*

The effect of pH on the extraction of iron(II) complex was examined. A constant absorbance was obtained over wider pH range from 5.0 to 9.3. Acetate buffer was finally chosen for pH adjustment; the absorbance was constant for the addition of 2 to 15 ml of 0.1 M solution (pH 5.5). A constant absorbance was also obtained by adding 1.5 to 5.0 ml of 0.05% TAMP solution for 20 μg of iron. Though 2 ml of 0.05% TAMP solution was used in practice, the amount corresponds to 12 times molar excess to that of iron.

*Effect of reducing agent and organic solvent*

It is necessary to fix the oxidation number of iron to iron(II), because the iron(III) complex extracted shows a weak color. The addition of ascorbic acid was effective for this purpose and a constant absorbance was obtained by adding 1 to 10 ml of 0.1% solution. The iron(II) complex was effectively extracted into such polar solvents as chloroform, 1,2-dichloroethane, ethyl acetate and nonpolar solvents as carbon tetrachloride (799 nm, $\varepsilon=1.59\times10^4$ l $mol^{-1}$ $cm^{-1}$), carbon disulfide (808 nm, $1.68\times10^4$) and benzene (797 nm, $1.63\times10^4$). Chloroform was used in practice, because of its fine phase separation and ease of use.

*Effect of other experimental variables*

The effect of aging time of the complex was examined and a constant absorbance was obtained by standing longer than 1 min after addition of TAMP solution. The complex was quantitatively extracted by shaking more than 30 s and the extracted species was stable for at least 3 h. The extract also showed a constant absorbance by the volume ratio ($V_{aq}/V_{org}$) up to 15. The composition of the complex was determined to be Fe(II):TAMP=1:2 by the continuous variation method. The complex may be an inner complex of the six-coordinate octahedral type, because thiazolylazo dyes usually act as tridentate ligands.[2]

*Calibration curve*

The calibration curve obeys Beer's law through the origin up to 50 μg of iron in 10 ml of chloroform. The molar absorptivity and Sandell's sensitivity for log ($I_0/I$)=0.001 are $1.54\times10^4$ l $mol^{-1}$ $cm^{-1}$ and $3.62\times10^{-3}$ μg $cm^{-2}$; such values indicate more sensitivity than those of the most reagents[8], such as 1,10-phenanthroline and 8-hydroxyquinoline. The relative standard deviation of

the absorbance in 10 measurements was 0.37% for 2.0 ppm of iron.

*Effect of diverse ions*

The effect of diverse ions on the determination of iron is summarized in Table 1, where the tolerance limit is set to ±5% for iron recovery. As the present method utilizes the specific absorption, the selectivity considerably increased compared with the case for other azo compounds. Iron can be determined in the presence of more than 10 ppm each of 39 metal ions, where metal ions generally present in natural waters, such as alkaline earths, aluminum and zinc, are tolerable even in large amounts. Amongst the anions examined, tartrate and citrate can also serve as masking agents.

*Determination of dissolved iron in river water*

The proposed method does not require the separation of iron as hydroxide, whereas the 1,10-phenanthroline method does.[9] The method was applied successfully to the determination of dissolved iron in river waters. The samples were filtered through a filter paper (No. 5C) immediately after collection, acidified with hydrochloric acid, and the aliquot was analyzed. The results agreed well with those obtained by AAS, as shown in Table 2.

Table 1 Effect of diverse ions on the determination of iron (2.0 μg Fe ml$^{-1}$)

| Ions | Tolerance limit, ppm |
|---|---|
| $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Al^{3+}$, $Zn^{2+}$, $Ga^{3+}$, As(V), Tl(I), $Na^+$, $K^+$, $NH_4^+$ | 1000 |
| $Cd^{2+}$, $Pb^{2+}$, $Th^{4+}$, Se(IV) | 500 |
| $Mn^{2+}$, $Bi^{3+}$, $Au^{3+}$, $Hg^{2+}$, $Ag^+$, $Mg^{2+}$, W(VI), Mo(VI), U(VI), Rh(IV), $Cu^{2+}$,[a] $Ni^{2+}$,[a] $Co^{2+}$[b] | 100 |
| $Pd^{2+}$ $Hf^{4+}$, V(V), Zr(IV), Sb(V), Ru(III) | 20 |
| $Sn^{4+}$, $Ti^{4+}$, $In^{3+}$, $Ge^{4+}$, Cr(VI), Te(VI) | 10 |
| $Cl^-$, $Br^-$, $I^-$, $NO_3^-$, $SO_4^{2-}$, $S_2O_3^{2-}$, $PO_4^{3-}$, $ClO_4^-$, acetate, tartrate | 50000 |
| $CO_3^{2-}$, $F^-$, thiosemicarbazide, dimethylglyoxime, citrate | 2000 |

a. One ml of 1% thiosemicarbazide solution added.
b. Two ml of 0.5% dimethylglyoxime solution added.

Table 2 Determination of iron in river waters

| Sample[a] | Sample taken/ml | Found/μg ml$^{-1}$[b] |
|---|---|---|
| Sai river | | |
| Uchikawa | 100 | 0.059(0.054) |
| Okuwa | 100 | 0.075(0.078) |
| Outfall | 50 | 0.332(0.340) |
| Tedori | | |
| Fukuoka | 100 | 0.057(0.060) |
| Kawakita | 100 | 0.064(0.068) |
| Outfall | 50 | 0.254(0.260) |

a. The waters sampled on March 15th, 1987.
b. Average of three separate determinations. Values obtained by AAS are given in parentheses.

*Extraction equilibrium of iron(II)-TAMP complex*

When $pK_{a1}$ (−0.3) <pH<$pK_{a2}$ (8.13)[2], most of TAMP is present in chloroform, and the iron(II) complex formed is also readily extracted into chloroform phase. If auxiliary ligands do not participate in the chelate, the extraction equilibrium can be expressed as

$$Fe^{2+}+2HR_{(o)} \rightleftharpoons FeR_{2(o)}+2H^+,\ K_{ex}=\frac{[FeR_2]_o[H^+]^2}{[Fe^{2+}][HR]_o^2} \quad (1)$$

From Eq. (1), Eq. (2) can be derived:

$$\log K'_{ex}=\log\frac{[FeR_2]_o}{[Fe^{2+}][HR]_o^2}=\log K_{ex}+2pH \quad (2)$$

The value of log $K'_{ex}$ can be calculated by the measurement of the absorbance of $[FeR_2]_o$. The plots of log $K'_{ex}$ against pH ranging from 3 to 5 showed a good linearity with a slope of 1.96, which indicates that Eq. (1) is reasonable. The extraction constant (log $K_{ex}$) was calculated to be −2.50±0.12 that is larger than other thiazolylazo dyes.[3,4]

*Kinetics of iron(II) extraction*

The extraction mechanism of iron(II) complex was kinetically examined under the pseudo-first order condition. The rate of the complex formation can be expressed as

$$-d[Fe^{2+}]/dt=k'[Fe^{2+}]^a[HR]_o^b[H^+]^c[H_2Y]^d \quad (3)$$

where $t$ is the reaction time, $k'$ is the rate constant, and a, b, c and d are the reaction orders with respect to the concentrations of $Fe^{2+}$, TAMP, $H^+$ and ascorbic acid, respectively. When iron was extracted with changing the concentration of TAMP, the plots of $([Fe^{2+}]_{t=0}/[Fe^{2+}]_{t=t})$ *versus* $t$ were all linear through the origin, which indicates that the complexation reaction is first order regarding iron concentration. Figure 2 shows the plots of $k_{obsd}$ *versus* log$[HR]_o$ and log$[H_2Y]$, respectively. From the slopes of the figures, we obtained the reaction orders of each species, *i.e.*, $b$=1.02±0.08, $c$=−1.06±0.05 and $d$=0. Since the major forms of TAMP and ascorbic acid present in aqueous phase in the pH range studied are HR, $R^-$ and $HY^-$ ($pK'_{a1}$= 4.03)[10], respectively, the equilibria and the reactions involved in the formation of monoiron complex are shown in Eqs. (4)-(8):

$$HR \rightleftharpoons HR_{(o)} \quad K_D=[HR]_o/[HR] \quad (4)$$

$$HR \rightleftharpoons H^+ + R^- \quad K_{a2}=[H^+][R^-]/[HR] \quad (5)$$

$$FeHY^+ + H^+ \xrightarrow{[K'_{a1}\beta_{FeHY^+}]^{-1}} Fe^{2+}+H_2Y \quad (6)$$

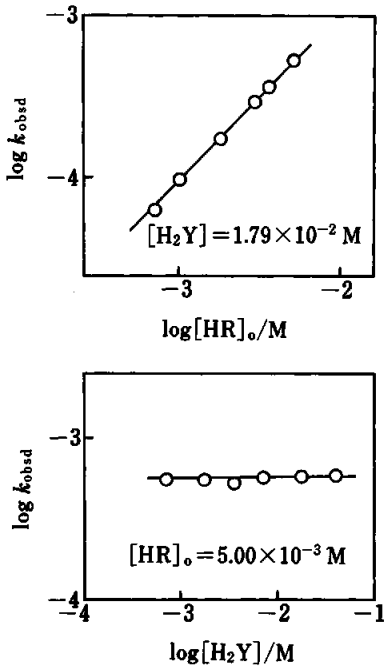


Fig. 2 Plots of log $k_{obsd}$ *vs.* log$[HR]_o$ and log$[H_2Y]$. Fe, $3.58\times10^{-4}$ M; pH=5.00; $\mu$=0.1(KCl); temperature, 25±0.1°C.

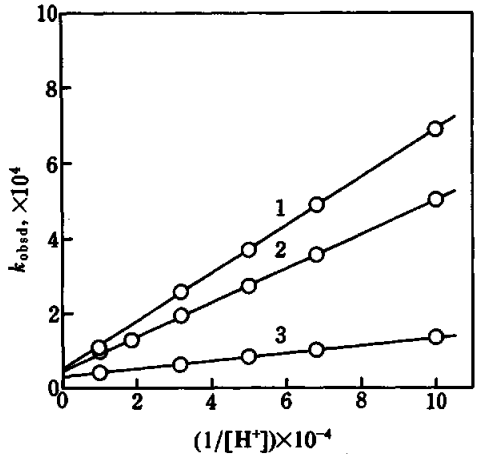


Fig. 3 Plots of $k_{obsd}$ *vs.* $1/[H^+]$ at different temperatures. Fe, $3.58\times10^{-4}$ M; $[HR]_o$, $5.00\times10^{-3}$ M; $[H_2Y]$, $1.79\times10^{-2}$ M; $\mu$=0.1(KCl). 1, 30°C; 2, 25°C; 3, 10°C.

$$Fe^{2+}+HR \xrightarrow{k_{HR}} FeR^{+}+H^{+} \quad (7)$$

$$Fe^{2+}+R^{-} \xrightarrow{k_R} FeR^{+}. \quad (8)$$

$K_D$ is the distribution constant of TAMP and $\beta_{FeHY}$ is the formation constant of the 1:1 complex with ascorbic acid. $k_{HR}$ and $k_R$ represent the rate constants of respective reaction steps. As ascorbic acid did not affect the extraction rate and the formation of the 1:1 iron complex is rate-determining, the rate equation of this extraction system can be expressed as

Table 3 Kinetic[a] and thermodynamic parameters[b] for complexation reaction of iron(II) with TAMP in the presence of ascorbic acid ($\mu$=0.1)

| | $k_R$ | $k_{HR}$ |
|---|---|---|
| 10°C | $2.49\times10^5$ | 57.5 |
| 25 | $1.07\times10^6$ | 78.6 |
| 30 | $1.50\times10^6$ | 86.2 |
| $E_a$ (kJ mol$^{-1}$) | 65.3 | 15.9 |
| $\Delta H^*$ (kJ mol$^{-1}$) | 62.8 | 13.5 |
| $\Delta G^*$ (kJ mol$^{-1}$) | 38.6 | 62.2 |
| $\Delta S^*$ (J K$^{-1}$ mol$^{-1}$) | 81.2 | −164 |

a. l mol$^{-1}$ S$^{-1}$.
b. Calculated at 25°C.

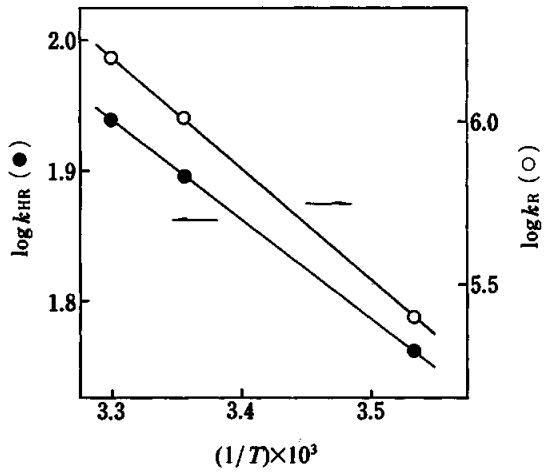


Fig. 4 Arrehenius' plots of log $k_R$ and log $k_{HR}$.

$$-d[Fe^{2+}]/dt = k_R[Fe^{2+}][R^-]+k_{HR}[Fe^{2+}][HR] = \left(k_R\frac{k_{a2}}{[H^+]}+k_{HR}\right)\frac{[Fe^{2+}][HR]_o}{K_D} \quad (9)$$

$k_R$ and $k_{HR}$ are obtained from the slope and the intercept of the linear plots in Fig. 3, respectively, and the results at different temperature are summarized in Table 3. The values of $k_R$ are $10^3-10^4$ order greater than those of $k_{HR}$, which indicates that the major extraction rate-determining step is a 1:1 complex formation reaction between $Fe^{2+}$ and dissociated TAMP. These values are $10-10^2$ order larger than those of $Fe^{2+}$ with water-soluble hydrazones.[11,12] Figure 4 shows the temperature dependence of the rate constants in the range of 10–30°C. The activation parameters at 25°C calculated from Arrhenius' plots are also summarized in Table 3. The parameters indicates that a 1:1 iron(II) complex formation is stabilized by passing over the energy barrier with large endothermic enthalpy change, but the process accompanied irregular nature, especially in $k_R$. The value of $k_R$ is almost compatible with the substitution rate constant of water molecule of $Fe^{2+}$-($k_{H_2O}=3\times10^6$ S$^{-1}$).[13] This suggests that the real rate-

determining step is the dissociation process of water molecule from $Fe^{2+}$ and that the outer-sphere complex as evaluated by Fuoss[14] plays only a small contribution in this extraction system. Consequently, ascorbic acid can act as a reducing agent, but exercises little influence to the extraction rate of the iron(II)-TAMP complex.

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