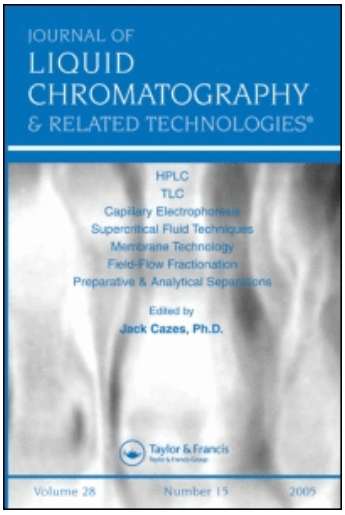


**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Selective Determination of Iron Ion in Tap Water by Solvent Extraction with 3,4-Dihydro-3-hydroxy- 4-oxo-1,2,3-benzotriazine, Followed by Reversed Phase HPLC

Susumu Ichinoki[a]; Shogo Fujita[a]; Youichi Fujii[a]
[a] Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan

Online publication date: 27 August 2010

**To cite this Article** Ichinoki, Susumu , Fujita, Shogo and Fujii, Youichi(2009) 'Selective Determination of Iron Ion in Tap Water by Solvent Extraction with 3,4-Dihydro-3-hydroxy- 4-oxo-1,2,3-benzotriazine, Followed by Reversed Phase HPLC', Journal of Liquid Chromatography & Related Technologies, 32: 2, 281 — 292
**To link to this Article: DOI:** 10.1080/10826070802603377
**URL:** http://dx.doi.org/10.1080/10826070802603377

*Journal of Liquid Chromatography & Related Technologies*®, 32: 281–292, 2009

ISSN: 1082-6076 print/1520-572X online
DOI: 10.1080/10826070802603377

# Selective Determination of Iron Ion in Tap Water by Solvent Extraction with 3,4-Dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine, Followed by Reversed Phase HPLC

**Susumu Ichinoki, Shogo Fujita, and Youichi Fujii**

Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan



**Abstract:** A selective determination method for Iron (Fe) ion in tap water has been developed by solvent extraction, followed by reversed phase HPLC with photometric detection. The Fe(III) ion was quantitatively extracted into chloroform over the pH range of 3.2 to 4.3 as 3,4-dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine (DHOB) chelate. Job's method indicated that the Fe-DHOB chelate composition was $Fe(DHOB)_3$. The molar absorptivity of the Fe-DHOB chelate was calculated as $7.6 \times 10^3$ at 430 nm. The extracted Fe-DHOB chelate was then separated on a phenyl column with an eluent of methanol/water/0.05 M DHOB (40:20:40, v/v) and detected at 500 nm. The correlation coefficients of the calibration curves obtained with 5 mL Fe standards were about 0.999 over the range of 10 ng/mL (ppb) to 10 μg/mL (ppm). The detection limit of the Fe ion in 5 mL water was estimated as 7 ppb, which corresponded to 3 times the standard deviation of the blank peak area. Effects of foreign ions on the determination of 0.2 ppm Fe ion were investigated with 57 metal ions. Almost none of the ions interfered, except for V(V), Sn(II), and Ti(IV) ions. The recovery with a spiked tap water sample for 0.5 ppm Fe ion ($N = 4$) was $99.2 \pm 0.9\%$.

**Keywords:** 3,4-Dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine, High performance liquid chromatography (HPLC), Iron (Fe) ion, Photometric detection, Solvent extraction, Tap water

Correspondence: Susumu Ichinoki, Faculty of Pharmaceutical Sciences, Hokuriku University, Ho 3, Kanagawa-machi, Kanazawa, Japan. E-mail: s-ichinoki@hokuriku-u.ac.jp

## INTRODUCTION

Atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are routinely used for metal analysis. Inductively coupled plasma-mass spectrometry (ICP-MS) is also used for more sensitive metal analysis. However, ICP-AES and ICP-MS require expensive instrumentation, and the detection sensitivity of AAS and ICP-AES varies considerably according to the metal. On the other hand, the application of high performance liquid chromatography (HPLC) for the separation and determination of metal ions has increased in recent years.[1–5] HPLC is very popular and not as expensive an apparatus; the running cost is very low. In addition, operation of the HPLC is easy, and a more sensitive quantitative analysis is possible by combining precolumn derivatization HPLC with a simple solvent extraction. We also determined various metal ions by HPLC as metal chelates[6–10] combined with solvent extraction and spectrophotometric detection.

We found that 3,4-dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine (DHOB) reacted with a Fe(III) ion, and the Fe-DHOB chelate was extracted into chloroform from a weak acidic solution. In addition, the Fe chelate was stable in chloroform. However, the analytical application of the DHOB is not found.

In this paper, analytical conditions, such as extraction pH, shaking time, and eluent composition, were studied for selective and sensitive determination of the Fe ion by reversed phase HPLC combined with solvent extraction. The molar absorptivity and chelate composition of Fe-DHOB chelate were also determined. In addition, the linearity of calibration curves and the detection limit of the Fe ion were investigated. Effects of foreign ions on the determination of the Fe ion were also investigated with 57 metal ions. The HPLC method was applied to determination of the Fe ions in a tap water sample.



## EXPERIMENTAL

### Instrumentation

The HPLC system consisted of a Jasco PU-1580i inert pump (Japan Spectroscopic Co., Ltd, Tokyo, Japan), a Rheodyne 9725i injector (Cotati, CA) equipped with a 200 μL sample loop of polyether etherketone (PEEK), an SPD-10AVvp photometric detector (Shimadzu Co., Kyoto, Japan), a Cosmosil 5-Ph PEEK column (Ph: phenyl, 250 × 4.6 mm ID, 5 μm particle, Nacalai Tesque, Kyoto, Japan), a Shimadzu Chromatopac C-R8A integrator, and a Thermo Minder SX-10R thermostat water bath (Taitec Co., Koshigaya, Japan). All HPLC units were

connected with the PEEK tubes. An MS-E10R microsyringe (10 μL) with Ni-Ti alloy plunger was used for sample injection (Ito. Co. Ltd., Fuji, Japan). A Yamato SA-31 auto shaker (Yamato Scientific Co., Ltd., Tokyo, Japan) was used for solvent extraction. A Shimadzu UV-1200 spectrophotometer and a 1 cm quartz cell were used for the visible spectrum of Fe-DHOB chelate. Micropipettes were used for 1 mL or less volume of solutions.

## Reagents

All reagents used were of analytical reagent grade unless otherwise stated. Milli-Q water was used for aqueous solution preparation and the extraction procedure. The chelating reagent DHOB (CAS No. 28230-32-2) was obtained from Tokyo Kasei Kogyou Co., Ltd. (Tokyo, Japan). Further details of the DHOB are shown in Figure 1. The DHOB was dissolved in ethanol in a concentration of 0.05 mol/L (M). The 58 metal standard solutions of 1000 ppm used were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). The Fe standard of 1000 ppm consisted of Fe and 0.2 M $HNO_3$. The other Fe solutions were prepared by dilution of the above solution (1000 ppm) with 0.1 M $HNO_3$. Methanol was distilled and filtered through a membrane filter (pore size, 0.45 μm). Acetate buffer solutions (pH 3.0–6.0) were prepared with 2 M acetic acid and 2 M sodium acetate solutions. Hydrochloric acid acetic acid solutions (pH 2.0 and 2.5) were prepared with 1 M hydrochloric acid and 1 M acetic acid. Hot water was collected from a gas water heater. Usual city water is introduced into a gas water heater and heated by a gas flame, and hot water emerges through a stainless steel tube. After cooling, the tap water was used as the tap water sample.



## Recommended Extraction Procedure and HPLC Conditions

Transfer 4 mL of sample solution and 1000 μL of 0.1 M $HNO_3$ into a 10 mL centrifuge tube with a stopper. For calibration curves, transfer a

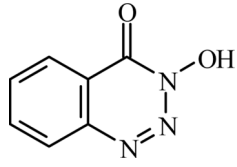


***Figure 1.*** 3,4-dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine (DHOB). $C_7H_5N_3O_2 =$ 163.14, CAS No. 28230-32-2.

Fe standard solution (0.1 M $HNO_3$) and 0.1 M $HNO_3$ (total volume 1000 μL) along with 4 mL of water into a centrifuge tube. Add 2 mL of 2 M acetate buffer solution (pH 3.5) to the centrifuge tube. After mixing the contents, add 500 μL of 0.05 M DHOB ethanol solution and 500 μL of chloroform into the tube (1000 μL chloroform for 1 to 10 ppm Fe). Shake the contents for 10 min and after standing for 10 min, collect the organic layer. Determine the Fe-DHOB chelate under the following HPLC conditions. Column: Cosmosil 5-Ph PEEK column (250 × 4.6 mm ID, particle size 5 μm), column temp.: 40°C, eluent: methanol/water/0.05 M DHOB (40:20:40, v/v), flow rate: 1.0 mL/min, injection volume of organic layer: 5 μL, detection wavelength: 500 nm.

## Screening Test for 58 Metal Ions

To a 10 mL centrifuge tube, 20 μL of each metal solution of 1,000 ppm, 0.5 mL of 1 M $HNO_3$, 5 mL of water, 500 μL of 0.05 M DHOB, and 500 μL of 4-methyl-2-pentanone were added. After shaking for 20 min, the organic layer was separated and used for HPLC analysis. The HPLC conditions used were as follows: column, Cosmosil 5 $C_{18}$-MS stainless steel column (150 × 4.6 mm ID); eluent, methanol/water/0.05 M DHOB (84:15:1, v/v); detection, 254 nm. The other conditions are the same as the recommended HPLC conditions. A blank test was also conducted, and the chromatographic peaks were compared.



## Visible Absorption Spectrum of Fe-DHOB Chelate

A 4.0 mL of water, 500 μL of 50 ppm Fe (Fe: 25 μg, 0.448 μmol) standard solution, 500 μL of 0.1 M $HNO_3$, 2.0 mL of 2 M acetate buffer solution (pH 3.5), 500 μL of 0.05 M DHOB, and 2.0 mL of chloroform were added to a 10 mL centrifuge tube. Two sample solutions were prepared, and the two organic layers were combined after shaking for 10 min. For a blank solution, 500 μL of 0.1 M $HNO_3$ was added instead of 500 μL of 50 ppm Fe standard. The visible absorption spectrum of the Fe-DHOB chelate was measured with the organic layers of standard and blank solutions.

## Chelate Composition of Fe-DHOB Chelate

To a 10 mL centrifuge tube, $x$ μL of $5.0 \times 10^{-3}$ M (279 ppm) Fe standard solution, $(1000-x)$ μL of 0.1 M $HNO_3$, 4 mL of water, 2000 μL of 2 M acetate buffer solution (pH 3.5), $y$ μL of $5.0 \times 10^{-3}$ M DHOB ethanol

solution, $(1000-y)$ μL of ethanol, and 1000 μL of chloroform were added. After shaking for 20 min, each organic layer was chromatographed, and the peak area of the Fe-DHOB chelate was measured. Where, $(x, y)$ were (0, 1000), (100, 900), (200, 800), (250, 750), (300, 700), (400, 600), (500, 500), (600, 400), (700, 300), (800, 200), (900, 100), and (1000, 0). The mole fractions of [Fe]/([Fe] + [DHOB]) were 0, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively.

### Effects of Foreign Ions

The effects of foreign ions on the determination of the Fe(III) ion were tested with 57 metal ions. Each foreign ion, 300 μL of 0.1 M $HNO_3$, and 200 μL of 5 ppm Fe standard were placed into a centrifuge tube, and diluted to 5 mL with water (Fe concentration: 0.2 ppm). The concentration of the Fe ion in the solution was determined by the recommended procedure. The recovery percentage was calculated from the peak area of the Fe chelate and that of the Fe standard (0.2 ppm) containing no foreign metal ions. The tolerance limit value of the foreign ion concentration was taken as the value that caused an error of less than 10% in the recovery of the Fe ion.



### Determination and Recovery Test of Fe with a Tap Water Sample

A 4.0 mL of a tap water sample and 1.0 mL of 0.1 M $HNO_3$ were added to a centrifuge tube. To another centrifuge tube, 4.0 mL of a tap water sample, 500 μL of 5 ppm Fe standard, and 500 μL of 0.1 M $HNO_3$ were added. The Fe concentrations in these solutions were determined according to the recommended procedure, and the recovery percentage was calculated.

## RESULTS AND DISCUSSION

### HPLC Conditions

The screening test for 58 metal ions indicated that Fe and vanadium(V) ions were extracted into the organic layer from acidic solution as colored chelates: Fe, orange; V, yellow. However, each organic layer gave no chromatographic peak of the DHOB chelate under the HPLC conditions used. For quantitative elution of Fe-DHOB chelate, a higher concentration of the DHOB was required in the eluent. However, the higher the DHOB concentration, the larger the blank peak. Consequently, the effect

of the DHOB concentration on the peak area of Fe-DHOB chelate was investigated with the Cosmosil 5Ph PEEK column and 5 mL of 1 ppm Fe standard. Constant peak areas were obtained in the range of 10 to 20 mM in eluent. Thus, the eluent of methanol/water/0.05 M DHOB (40:20:40, v/v) was employed. Typical chromatograms of the Fe-DHOB chelate and blank are shown in Figure 2.

The peak areas of standard and blank were measured at 440–540 nm. Detection wavelength was set at 500 nm, which gave the maximum peak area ratio of standard to blank. In these conditions, the V ion gave a small chromatographic peak compared with the Fe ion.

The metal free PEEK column is recommended for sensitive detection of the Fe ion because the column consists of the PEEK tube and ceramic frits.



## Extraction Conditions

At first, Fe-DHOB chelate was extracted into 4-methyl-2-pentanone. However, it was found that chloroform was superior in solubility of the Fe-DHOB chelate. Thus, chloroform was employed as extraction solvent. However, 5 ppm or more concentration of Fe ion resulted in

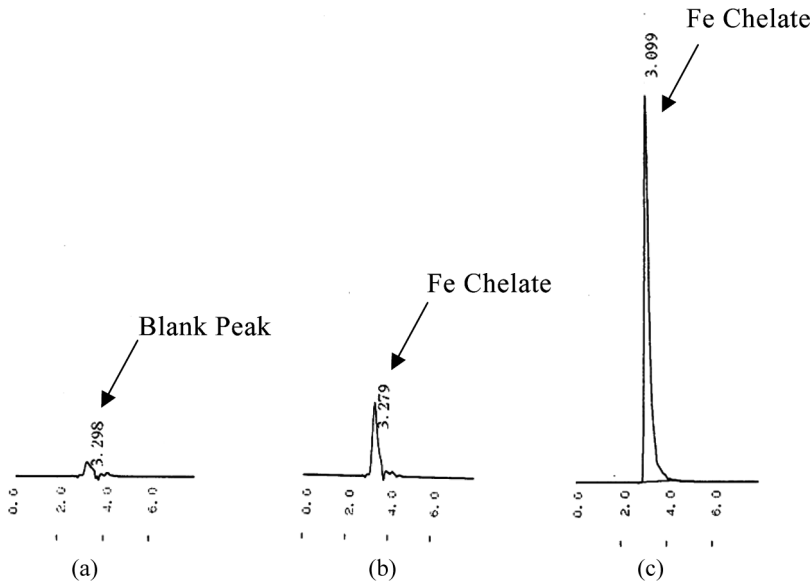


***Figure 2.*** Chromatograms of blank and Fe-DHOB chelate. a) blank, b) 0.1 ppm Fe, c) 1.0 ppm Fe.

an orange precipitation in the chloroform layer. Thus, 1000 μL chloroform was used for 1 to 10 ppm Fe ion solution.

Extraction pH was investigated with 1 ppm Fe standard and various buffer solutions according to the recommended procedure. After extraction, the pH of each aqueous layer was measured. The peak area of the Fe-DHOB chelate was plotted against the measured pH. The effect of pH on extraction of the Fe-DHOB chelate is shown in Figure 3. As constant peak areas were obtained over the pH range of 3.2 to 4.3, 2 mL of 2 M acetate buffer solution of pH 3.5 was used in the recommended extraction procedure. When the buffer solution of pH 3.5 was used, the Fe(III) ion was quantitatively extracted into the chloroform by shaking for 5–60 minutes. Subsequently, 10 min was selected as the shaking time.

The extracted Fe-DHOB chelate in the chloroform was found stable for at least 7 hours, because the peak areas of the Fe-DHOB chelate were almost constant. Thus, immediate injection of the organic layer was not required.



## Fe-DHOB Chelate Composition

The composition of the Fe-DHOB chelate was investigated by Job's method. The peak areas were plotted against the mole fractions of [Fe]/([Fe]+[DHOB]) as shown in Figure 4. The maximum peak area was obtained at a mole fraction of 0.25 (that is [Fe]:[DHOB] = 1:3). The results indicated that the DHOB ionized to $H^+$ and $DHOB^-$, then reacted with the $Fe^{3+}$ ion to form $Fe(DHOB)_3$ chelate.

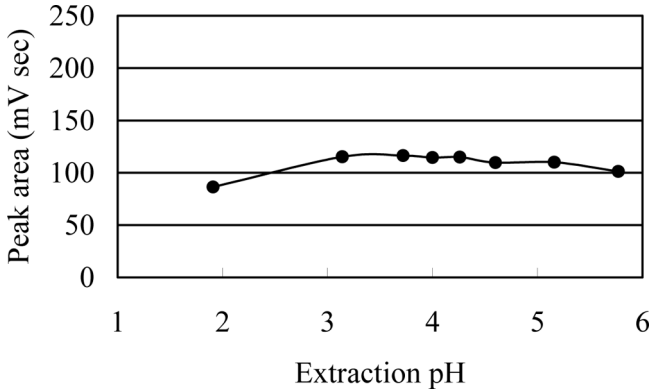


*Figure 3.* Effect of pH on extraction of Fe-DHOB chelate. Each pH of the aqueous phase was measured by a pH meter after shaking for 10 min.

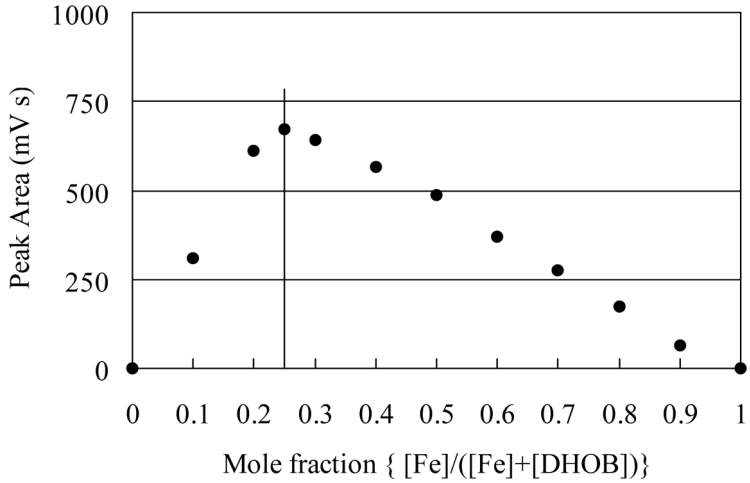


***Figure 4.*** Determination of Fe-DHOB chelate composition by Job's method. Experimental conditions are in the text.



## Visible Absorption Spectrum of Fe-DHOB Chelate and Molar Absorptivity

The visible absorption spectrum of the Fe-DHOB chelate is shown in Figure 5. Maximum absorption wavelength was 430 nm. When Fe ion

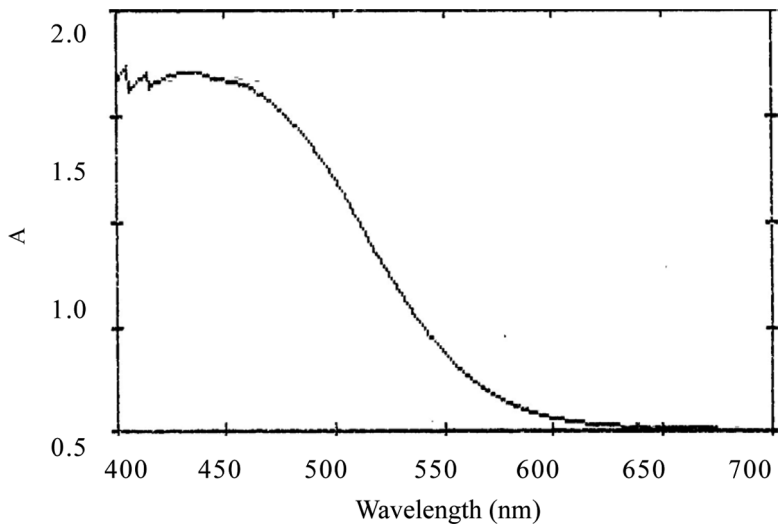


***Figure 5.*** Visible spectrum of Fe-DHOB chelate. Concentration of Fe-DHOB chelate in chloroform was $2.25 \times 10^{-4}$ M. A is absorbance.

was quantitatively extracted into chloroform, the concentration of Fe-DHOB chelate was calculated as $2.25 \times 10^{-4}$ mol/L. Figure 5 shows that the absorbance at 430 nm is 1.7. Accordingly, the molar absorptivity ($\varepsilon$) of the Fe-DHOB chelate was calculated as $7.6 \times 10^3$ from Lambert-Beer's law ($1.7 = \varepsilon \times 2.25 \times 10^{-4}$ mol/L $\times$ 1 cm).

## Calibration Curves, Repeatability, and Detection Limit

Calibration curves for the Fe(III) ions were prepared with the Fe standards of varying concentrations by the recommended procedure. The correlation coefficients of the calibration curves obtained with 5 mL Fe standards were about 0.999 over the range of 0.01 ppm (10 ppb) to 10 ppm. Repeatability of the peak areas for 5, 0.5, and



***Table 1.*** Calibration curves for Fe(III) ion and repeatabilities of peak areas

*Calibration curves for Fe ion*

| Concentration range | Equation of line | Correlation coefficient | Measuring point (ppm) |
|---|---|---|---|
| 1–10 ppm | $y = 60.815x + 0.3298$[a] | 0.9999 | 0, 1, 2, 4, 6, 8, 10 |
| 0.1–1 ppm | $y = 126.03x + 0.6788$[b] | 0.9997 | 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 |
| 0.01–0.1 ppm | $y = 122.18x + 6.1306$[b] | 0.9987 | 0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10 |

*Repeatabilities of peak areas (mV sec)*

| 5 ppm Fe | | 0.5 ppm Fe | | 0.05 ppm Fe | |
|---|---|---|---|---|---|
| No. of run | Peak area | No. of run | Peak area | No. of run | Peak area |
| 1 | 334.128 | 1 | 79.096 | 1 | 11.454 |
| 2 | 338.100 | 2 | 80.548 | 2 | 11.240 |
| 3 | 336.353 | 3 | 78.718 | 3 | 11.283 |
| 4 | 335.683 | 4 | 79.512 | 4 | 11.134 |
| 5 | 336.857 | 5 | 79.619 | 5 | 11.148 |
| Average | 336.224 | Average | 79.499 | Average | 11.252 |
| SD[c] | 1.468 | SD[c] | 0.687 | SD[c] | 0.129 |
| RSD[d] (%) | 0.4 | RSD[d] | 0.9 | RSD[d] | 1.1 |

y: peak area (mV sec), x: concentration of Fe ion (ppm).

[a]Fe chelate was extracted into 1000 μL of chloroform.

[b]Fe chelate was extracted into 500 μL of chloroform.

[c]Standard deviation.

[d]Relative standard deviation.

The relative standard deviations of peak areas for 5, 0.5, and 0.05 ppm Fe standards obtained on another days were 0.7, 0.8, and 1.6%, respectively.

0.05 ppm Fe standards were also investigated. Relative standard deviations of the peak areas were less than 2%. More details are shown in Table 1.

The detection limit of the Fe ion in 5 mL water was estimated as 7 ppb, which corresponded to 3 times the standard deviation of the blank peak area. To reduce the blank value, a metal free column and iron free microsyringe are recommended.

## Effects of Foreign Ions

The effects of 57 foreign ions on the determination of 0.2 ppm Fe(III) ion (5 mL) are summarized in Table 2. Table 2 shows 47 metal ions did not interfere at 200 times (40 ppm) or more the concentration of the Fe ion. The V(V) ion of 0.4 ppm, 4 ppm Sn(II), and 10 ppm Ti(IV) interfered with the determination of the 0.2 ppm Fe ion. The V(V) ion was partly extracted into chloroform as DHOB chelate, and the peak overlapped with the Fe chelate peak. The Sn(II) standard contained 2.5 M hydrochloric acid, and Ti(IV) standard contained 2.0 M sulfuric acid. The high concentration acid probably interfered with the determination of the Fe ion. More details are shown in Table 2.



***Table 2.*** Effects of foreign metal ions on determination of 0.2 ppm Fe(III) ion

| Tolerance limit | Metal ion |
|---|---|
| 100 ppm | Al(III), Ba(II), Ca(II), Cs(I), Dy(III), Er(III), Gd(III), K(I), Mg(II), Mo(VI), Se(IV), Si(IV), Sr(II), Tl(I), Tm(III), Yb(III), As(III), Au(III), Cd(II), Co(II), Cr(VI), Ge(IV), In(III), Hg(II), Mn(II), Ni(II), Pt(IV), Rh(III), Zn(II), Pr(III), Na(I), Nd(III) |
| 40 ppm | Ag(I), Ce(III), Eu(III), Ho(III), La(III), Lu(III), Pb(II), Sb(III), Sc(III), Sm(III), Ta(V), Tb(III), Te(IV), Y(III), Zr(IV) |
| 20 ppm | Be(II), Nb(V), Pd(II), W(VI) |
| 10 ppm | Bi(III), Cu(II), Ga(III) |
| 4 ppm | Ti(IV) |
| 2 ppm | Sn(II) |
| 0.2 ppm | V(V) |

*Note*: The tolerance limit value of the foreign ion concentration was taken as the value that caused an error of less than 10% in the recovery of Fe(III) ion (0.2 ppm).

*Table 3.* Results of Fe(III) ion determination in tap water and recovery test

| No. of run | Sample[a] (ppm) | Added (ppm) | Found (ppm) | Recovery (%)[b] | Equation of calibration curve | Correlation coefficient |
|---|---|---|---|---|---|---|
| 1 | 0.254 | 0.500 | 0.750 | 99.8 | $y = 125.47x + 0.9573$ | 0.9995 |
| 2 | 0.237 | 0.500 | 0.746 | 99.1 | | |
| 3 | 0.263 | 0.500 | 0.741 | 97.9 | y: peak area (mV sec) | |
| 4 | | 0.500 | 0.751 | 100.0 | x: Fe conc. (ppm) | |
| Average | 0.251 | 0.500 | 0.747 | 99.2 | | |
| SD[a] | 0.013 | | 0.005 | 0.9 | | |
| RSD[b] | 5.2 | | 0.6 | 0.9 | | |

[a]Sample: Fe concentration in tap water.
[b]Recovery(%): (Found $-0.251) \times 100/0.5$.
Recovery obtained on other day was $100.7 \pm 2.2\%$ for 0.5 ppm Fe ($N = 4$).



### Determination and Recovery Test of Fe Ion with Tap Water Sample

The results of determination of Fe(III) ion in tap water and recovery test for 0.5 ppm Fe ions are summarized in Table 3. The correlation coefficients of the calibration curves were 0.9995. The recovery of 0.5 ppm Fe was $99.2 \pm 0.9\%$. Recovery obtained on another day was $100.7 \pm 2.2\%$ for 0.5 ppm Fe ($N = 4$). The high recovery indicated that the ions in tap water did not interfere with the HPLC determination of the Fe ion.

## CONCLUSION

The proposed extraction and HPLC procedure is simple and easy, and the HPLC apparatus used is the most popular HPLC apparatus equipped with a photometric detector. The extraction time and HPLC analysis time is 10 and 8 min, respectively. The DHOB was found to be a selective chelating reagent for ppm levels of Fe(III) ion. The HPLC method was applied to the determination of the Fe ion in tap water with precise results.

## REFERENCES

1. Timerbaev, A.R.; Petrukhin, O.M.; Zolotov, Y.A. Analytical application of liquid chromatography of metal chelates. Fresenius Z. Anal. Chem. **1987**, *327*, 87–101.
2. Robards, K.; Starr, P.; Patsalides, E. Metal determination and metal speciation by liquid chromatography. Analyst. **1991**, *116*, 1247–1273.
3. Wang, P.; Lee, H.K. Recent application of high-performance liquid chromatography to the analysis of metal complexes. J. Chromatogr. A. **1997**, *789*, 437–451.

4. Sarzanini, C. High performance liquid chromatography: Trace metal determination and speciation. Adv. Chromatogr. **2001**, *41*, 249–310.
5. Cecchi, T. Application of ion pairing chromatography to the analysis of inorganic analytes: Review. J. Liq. Chromatogr. & Rel. Technol. **2007**, *30*, 1205–1225.
6. Ichinoki, S.; Yamazaki, M. Simultaneous determination of nickel, lead, zinc, and copper in citrus leaves and rice flour by liquid chromatography with hexamethylenedithiocarbamates extraction. Anal. Chem. **1985**, *57*, 2219–2222.
7. Ichinoki, S.; Hongo, N.; Yamazaki, M. Multielement analysis by high-performance liquid chromatography following solvent extraction with acetylacetone. Anal. Chem. **1988**, *60*, 2099–2104.
8. Ichinoki, S.; Iwase, H.; Arakawa, F.; Hirano, K.; Fujii, Y. Selective determination of tin(II) ion in water by solvent extraction with salicylideneamino-2-thiophenol followed by reversed-phase high-performance liquid chromatography with photometric detection. J. Liq. Chromatogr. & Rel. Technol. **2003**, *26*, 3129–3139.
9. Ichinoki, S.; Miyanaga, S.; Hattori, M.; Fujii, Y. Selective determination of iron in river water and standard bovine liver by solvent extraction with *N*-Benzoyl-*N*-phenylhydroxylamine followed by reversed-phase HPLC. J. Liq. Chromatogr. & Rel. Technol. **2005**, *28*, 1417–1429.
10. Ichinoki, S.; Otani, S.; Fujii, Y. Selective determination of palladium ion in river water by solvent extraction with 5-chloro-2-mercaptobenzothiazole followed by reversed-phase HPLC. J. Liq. Chromatogr. & Rel. Technol. **2006**, *29*, 2457–2469.

Received July 9, 2008
Accepted July 23, 2008
Manuscript 6373