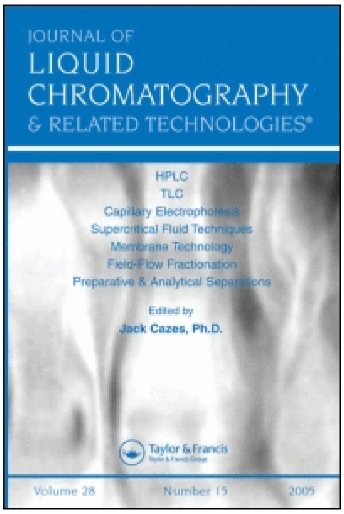

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Abstract: A simple and selective high performance liquid chromatographic method has been developed for the determination of total iron in water samples. 2-(8-quinolylazo)-4,5-diphenylimidazole (QAI) was used as a precolumn chelating reagent for iron(II). The iron(II)-QAI chelate was separated on a Cosmosil 5C8-MS column with an aqueous acetonitrile mobile phase containing tetrabutylammonium bromide and spectrophotometrically detected at 710 nm. Iron(III) was determined as the iron(II) chelate with QAI after it was reduced to iron(II) using ascorbic acid. Detection limit, defined as three times of standard deviation of a blank signal, was 18 pg of iron(II) in 100 μL injection. Total iron in environmental water samples was selectively determined without any pretreatment.

Keywords: HPLC, 2-(8-quinolylazo)-4,5-diphenylimidazole, Iron, Natural waters

INTRODUCTION

In an aquatic environment, the concentration of dissolved iron changes the biological availability of trace metals.[1] An iron deficiency found in some regions of the global oceans was hypothesized to have limited the phytoplankton growth. Experiments show that the addition of iron to such an ecosystem

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caused a massive phytoplankton bloom and an increase of nitrate and carbon uptake.[2–5] Martin et al. suggested that oceanic iron fertilization might be a feasible approach to remove the atmospheric carbon dioxide and moderate the global climate.[6] The determination of iron in natural waters is meaningful to reveal the biogeochemistry function of the essential element.

A number of analytical techniques, such as spectrophotometry,[7] chemiluminescence,[8,9] high performance liquid chromatography (HPLC),[10] capillary electrophoresis,[11] cathodic stripping voltammetry,[12,13] and inductively coupled plasma mass spectrometry[14,15] have been developed for the determination of trace levels of iron in environmental water samples. These methods have been always carried out with a preliminary concentration and separation, such as a column adsorption and a solvent extraction, because of the low iron concentration and the interference with many diverse ions in natural waters.

In this work, 2-(8-quinolylazo)-4,5-diphenylimidazole (QAI) is demonstrated as an effective precolumn chelating reagent for reversed phase HPLC separation of iron(II). The method is based upon the RP-HPLC separation of iron(II) chelate with QAI followed by the selective spectrophotometric-detection. The proposed method is successfully applied to the analyses of rainwater, river water, and springwater samples without preconcentration and preseparation.

EXPERIMENTAL

Apparatus

The chromatographic system was equipped with a Shimadzu LC-9A pump, a Rheodyne 7125 injector, and a Shimadzu SPD-10AV UV-visible spectrophotometric detector. The reversed phase separation column was a Cosmosil 5C8-MS (4.6 mm × 100 mm, Nacalai Tesque, Kyoto, Japan). A Shimadzu SPD-M10AVP photodiode array detector packed with a Class-LC10 data processor was used to obtain three-dimensional chromatograms of QAI and its metal chelates. Absorption spectra of QAI and its metal chelates were measured with a Shimadzu UV-260 spectrophotometer. The pH values were measured by a Toa Denpa HM-20E pH meter.

Reagents and Solutions

QAI was synthesized according to the method proposed by Shibata and coworkers.[16] A solution of 3.6×10^{-4} M QAI was prepared by dissolving it in 5% (m/v) POOE-10 solution. Standard metal ion solutions were obtained by diluting 100 mg L^{-1} solutions for atomic absorption spectrometry (Kanto Chemical Co., Inc., Japan) to the desired concentration with 0.2 mol L^{-1}

hydrochloric acid. Acetate buffer solution (pH 5.1) was prepared by dissolving sodium hydroxide in 1.0 mol L^{-1} of acetic acid solution. All aqueous solutions were prepared with high purity deionized water produced by a Millipore Milli-Q system and all reagents were used without further purification.

Recommended Procedure

A sample solution containing iron ion less than 220 ng was accurately weighed into a 30-mL screw-capped Teflon bottle. Then, 2 mL of 0.5% (m/m) ascorbic acid, 2 mL of acetate buffer (pH 5), and 1 mL of 3.6×10^{-4} M QAI solution (in 5% (m/v) POOE-10) were added, successively. The mixture was diluted to 25.00 g with water on the balance, and the test solution obtained was accurately weighed (W g). The bottle was tightly closed and heated on a boiling water bath for 10 min, and then cooled to room temperature. Before and after heating, the pH of the solution did not vary. The test solution, thus obtained, was injected onto the Cosmosil 5C8-MS column using a 100 μL loop injector. QAI and its metal chelates were separated with 58% (m/m) aqueous acetonitrile solution containing 1.0×10^{-4} mol kg^{-1} tetrabutylammonium bromide (TBABr), 2.0×10^{-3} mol kg^{-1} ethylenediamine tetraacetic acid (EDTA), and 5.0×10^{-3} mol kg^{-1} sodium acetate at a flow rate of 1.0 mL min^{-1}. Iron(II) chelate with QAI was selectively detected at 710 nm. Peak heights of iron(II) chelate measured on the chromatogram were corrected by multiplying these values by the dilution factor ($W/25.00$) of each corresponding test solution. The peak height corrected of the iron(II) chelate was proportional to the amounts of total iron in the test solution.

Environmental Water Samples

Rainwater was collected at the campus of University of Fukui. River water was sampled from Kuzuyru River in Fukui Pref. Springwater was obtained from Eiheiji in Fukui Pref. All sample containers were 500 mL polyethylene bottles, precleaned by soaking them in 5 mol L^{-1} nitric acid solution and rinsing with water. If the sample contains suspended particulates, it is necessary to filter it through a 0.45 μm membrane filter before analysis.

RESULTS AND DISCUSSION

Pre-Column Derivatization of Iron(II) with QAI

Dissolved iron in natural water is present in the divalent and tervalent states.[17] For determining total dissolved iron, iron(III) has to be reduced to iron(II); iron(III) was usually reduced to iron(II) by addition of hydroxylamine hydrochloride[8] and ascorbic acid.[7,9] Ascorbic acid was adopted in the proposed system because Elrod and coworkers recommended this reagent due to its efficient reduction power.[9] The reduction of 250 ng of iron(III) was successfully accomplished with 1.5–2.5 mL of 0.5% (m/m) ascorbic acid solution. Two milliliters of the solution was added to each sample prior to addition of QAI solution in the recommended procedure.

Iron(II), nickel(II), cobalt(II), zinc(II), manganese(II), copper(II), cadmium(II), and vanadium(V) react with QAI to form the chelates. The cobalt(II) chelate was easily oxidized to the positively charged cobalt(III) chelate in aqueous solutions. Among these chelates, the iron(II), cobalt(III), and nickel(II) chelates gave resolved peaks on the chromatogram, as shown below. Effects of nickel(II) and cobalt(III) should be examined for the selective determination of iron(II). Figure 1 shows absorption spectra of QAI and its metal chelates. QAI itself showed a maximum absorbance at 462 nm and the absorbance was constant in the pH range of 4–8. The nickel(II) and cobalt(III) chelates with QAI showed the maximum absorbances at 570–610 nm. The iron(II) chelate with QAI has absorption maxima at 729 nm and 608 nm in the measurement of the absorption spectra by a conventional spectrophotometer (here, a Shimadzu UV-260) and at 710 nm and 605 nm by a photodiode array detector used in HPLC (here, a Shimadzu SPD-M10AVP). The detection at 710 nm was chosen for the selective determination of iron(II) because QAI and the other chelates have no absorption at this wavelength.

The quantitative complexation between QAI and iron(II) was completed by heating the test solution on a boiling water bath for 10 min. The absorbance of iron(II) chelate with QAI was maximum and constant in the pH range of 4–8, as shown in Fig. 2. The pH of the test solution was adjusted to

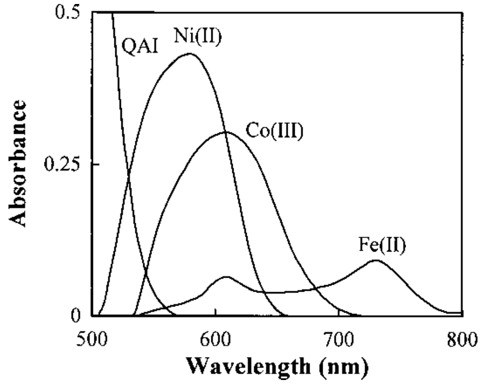

Figure 1. Absorption spectra of QAI and its metal chelates. Fe(II), Co(III), and Ni(II): 5.00 × 10^{-6} mol L^{-1}; QAI: 5.0 × 10^{-5} mol L^{-1}; pH 7.20 ± 0.05. Reference: water for QAI and reagent blank for metal-QAI chelates.

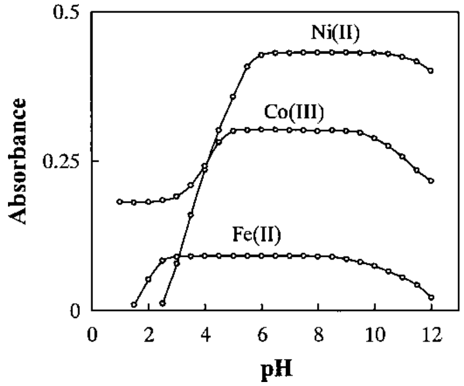

Figure 2. Influence of pH on absorbance of metal chelates with QAI. Fe(II), Co(III), and Ni(II): 5.00 × 10^{-6} mol L^{-1}, measured at 729 nm, 609 nm, and 581 nm, respectively; QAI: 5.0 × 10^{-5} mol L^{-1}. Reference: reagent blank.

5.0 ± 0.5 with the acetate buffer solution (pH 5.1) to keep the selective condition for the complexation of iron(II).

Chromatographic Separation and Detection of Iron(II) Chelate with QAI

The chromatographic separations were investigated using the standard test solution (25.00 g) containing each 200 ng of iron(III), nickel(II), cobalt(II), copper(II), zinc(II), cadmium(II), manganese(II), aluminum(III), and vanadium(V). The acetonitrile : water mobile phase was buffered at pH 7.5 ± 0.5 with EDTA and sodium acetate, which were 2.0 × 10^{-3} mol kg^{-1} and 5.0 × 10^{-3} mol kg^{-1}, respectively. EDTA was found to be a useful ligand to mask metal ion contaminants from the chromatographic system.

The elution of QAI and its metal chelates can be improved by varying the concentration of acetonitrile and TBABr in the mobile phase. The retention time of QAI and its chelates decreased with increasing concentration of acetonitrile. As shown in Fig. 3a, QAI, iron(II), nickel(II), and cobalt(III) were successively separated on the column by use of 58% (m/m) aqueous acetonitrile mobile phase. Figure 3b shows the effect of TBABr added to the mobile phase on the retention of QAI and its metal chelates. In both cases (Fig. 3a and 3b), QAI, iron(II), nickel(II), and cobalt(III) were detected by measuring at 605 nm. Without TBABr, the elution order was QAI < iron(II) < nickel(II) < cobalt(III); it took 15 min to finally elute the cobalt(III) chelate, (Fig. 3a). On the other hand, the elution of cobalt(III) chelate was accelerated by adding TBABr; the resultant order was QAI < iron(II) < cobalt(III) < nickel(II) (Fig. 3b); the whole elution time decreased to half (8 min) of that obtained in the absence of TBABr. A similar behavior was reported for

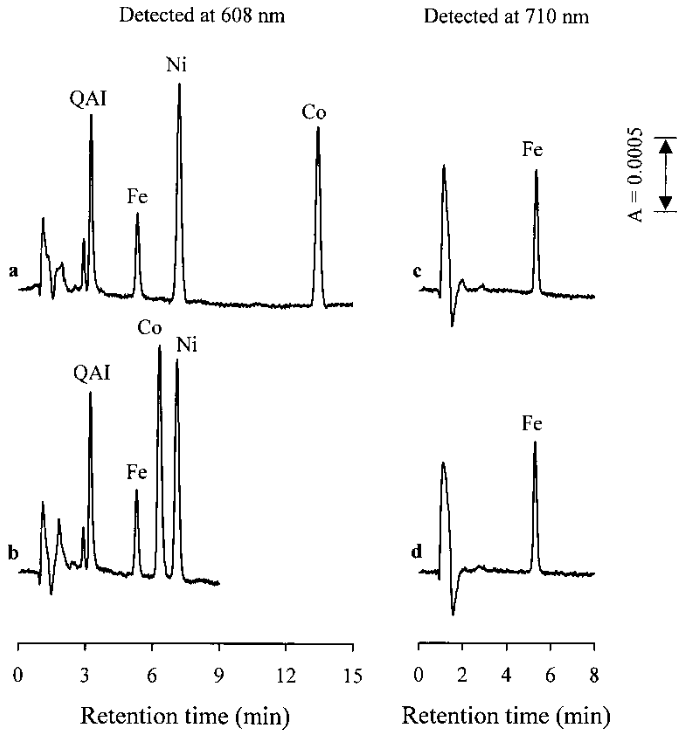

Figure 3. Chromatograms of QAI and its metal chelates with 58% (m/m) aqueous acetonitrile mobile phase in the absence of TBABr ((a) at 608 nm and (c) at 710 nm), and in the presence of 1.0×10^{-4} mol kg^{-1} TBABr ((b) at 608 nm and (d) at 710 nm). Injection volume: 100 μL. Flow rate: 1.0 mL min^{-1}. Column: Cosmosil 5C8-MS. Test solution: standard multielement solution containing each 200 ng of iron(III), nickel(II), cobalt(II), zinc(II), manganese(II), aluminum(III), copper(II), cadmium(II), and vanadium(V) in 25.00 g.

cobalt(III) chelate with other azo compounds.[18] This is due to the preferential adsorption of TBA^+ on the support by the hydrophobic interaction and ion exchange process.[18] As a result, the cobalt(III) chelate cation was excluded from the stationary phase, which was mostly covered by the TBA^+ cation. The addition of TBABr to the mobile phase is beneficial to maintain the analytical column and to prolong the lifetime of it, because the strong retention of the cobalt(III) chelate on the column was prevented.

At 710 nm, only iron(II) chelate was detected with a low background noise regardless of addition of TBABr, as shown in Fig. 3c and 3d. The monitoring at 710 nm was recommended for the highly selective and sensitive detection of the iron(II) chelate with QAI.

For the rapid, selective, and sensitive determination of iron(II), 58% (m/m) of acetonitrile mobile phase containing EDTA, sodium acetate and

1.0×10^{-4} mol kg^{-1} TBABr was used, and the measurement was carried out at 710 nm. In this case, only 8 min was needed for an analytical run in HPLC.

Calibration Curve and Sensitivity

The calibration curve was linear up to 220 ng of iron in the test solution (25.00 g). The detection limit for iron(II), which was defined as three times of standard deviation of the blank, was 4.5 ng in 25.00 g of the test solution (18 pg in 100 μL injection) at 0.001 absorbance unit full scale. The relative standard deviation for four determinations of 104 ng of iron(II) in 25.00 g of the test solution was 3.7%. The proposed method showed high sensitivity and good reproducibility for the determination of iron(II).

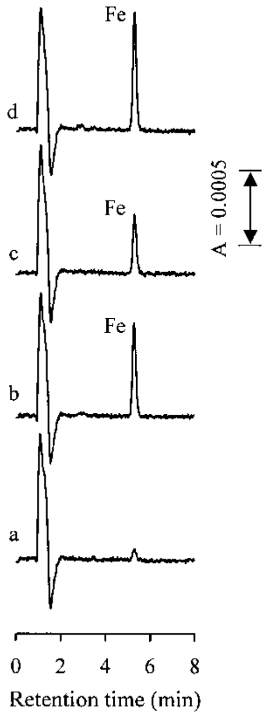

Figure 4. Chromatograms of standard solution and river water samples: (a) blank signal, (b) standard solution containing 150 ng of iron(III), (c) river water (1.50 g), (d) river water (1.5 g) spiked 100 ng of iron(III). Detection wavelength: 710 nm. Mobile phase: 58% (m/m) aqueous acetonitrile solution containing 1.0×10^{-4} mol kg^{-1} TBABr, 2.0×10^{-3} mol kg^{-1} EDTA, and 5.0×10^{-3} mol kg^{-1} sodium acetate. Injection volume, flow rate, and column as in Fig. 3.

Table 1. Determination of total iron in water samples

Sample	Weight of sample (g)	In 25.00 g of test solution: Fe added (ng)	Fe found[a] (ng)	RSD[b] (%)	Recovery (%)	Concentration (ng g^{-1})
Rainwater	6.00_0		90	7.2		15
(2004.12.26)	6.00_3	101	187	7.1	96	
River water	1.50_4		79	4.1		53
(2004.12.25)	1.50_1	100	174	4.2	95	
Springwater	3.50_3		107	1.0		31
(2004.10.16)	3.50_5	100	199	2.5	92	

Detection limit (defined as three times of standard deviation of a blank signal): 4.5 ng of iron(II) in 25.00 g of test solution.

[a] Average of three determinations.

[b] Relative standard deviation.

Application for Environmental Water Analysis

Three kinds of environmental water samples were analyzed according to the recommended procedure. Figure 4a shows the blank signal. Figure 4b, 4c, and 4d show the chromatograms of standard solution containing 150 ng of iron(III), river water, and river water spiked 100 ng of iron(III), respectively. The analytical results for total iron in rainwater, river water, and springwater are summarized in Table 1. Accuracy of the method was assessed by the standard addition recovery experiment. The recoveries calculated in all cases were in the range of 92–99%. Less than several grams or milliliters of natural water samples could be directly analyzed without any preseparation and preconcentration of iron ions.

QAI was an effective precolumn chelating reagent for the determination of iron(II). The proposed method is simple, highly selective, and highly sensitive and is useful for the determination of total iron in environmental water samples.

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