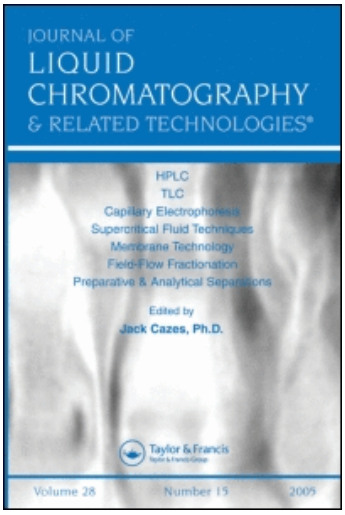

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Susumu Ichinoki[a]; Chie Onishi[a]; Youichi Fujii[a]
[a] Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan

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Selective Determination of Nickel Ion in River Water by Solvent Extraction with α-Furyl Dioxime, Followed by Reversed-Phase HPLC with Photometric Detection

Susumu Ichinoki, Chie Onishi, and Youichi Fujii
Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan

Abstract: A selective determination method for nickel (Ni) ion in river water has been developed by solvent extraction, followed by reversed-phase HPLC with photometric detection. The Ni(II) ion was quantitatively extracted into 4-methyl-2-pentanone over the pH range of 7.5 to 9.0 as α-furyl dioxime (FDO) chelate. The extracted Ni-FDO chelate was then separated on an ODS column with an eluent of methanol/water (85:15, v/v) and detected at 435 nm. Job's method suggested that the Ni-FDO chelate composition was $Ni(FDO)_2$. The molar absorptivity of the Ni chelate was determined as 1.7×10^4 at 435 nm. The correlation coefficients of the calibration curves obtained with 5 mL Ni standards were more than 0.999 over the range of 1 ng/mL (ppb) to 1 μg/mL (ppm). The detection limit of the Ni ion in 5 mL water was estimated as 0.8 ppb, which corresponded to 3 times the standard deviation of the blank peak area. Relative standard deviations of peak areas ($N = 6$) for 1 and 0.1 ppm Ni standards were less than 2%. The recoveries with a spiked river water sample for 500, 50, and 5 ppb Ni ion ($N = 5$) were $100.5 \pm 1.5\%$, $101.2 \pm 1.5\%$, and $97.5 \pm 6.4\%$, respectively. Effects of foreign ions on the determination of 0.05 ppm Ni ion were investigated with 57 metal ions. Almost none of the ions interfered, except for Rh(III), Co(II), and Sn(II) ions.

Keywords: α -Furyl dioxime, Nickel (Ni) ion, Solvent extraction, High performance liquid chromatography (HPLC), River water, Photometric detection

Address correspondence to Susumu Ichinoki, Faculty of Pharmaceutical Sciences, Hokuriku University, Ho 3, Kanagawa-machi, Kanazawa 920-1181, Japan. E-mail: s-ichinoki@hokuriku-u.ac.jp

INTRODUCTION

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

We found that α-furyl dioxime (FDO) reacted with a Ni(II) ion, and formed Ni-FDO chelate. The yellow Ni chelate was extracted into 4-methyl-2-pentanone from a weak alkaline solution. In addition, the Ni chelate was stable in a reversed-phase column in the absence of FDO in eluent. However, the analytical application of the FDO 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 Ni ion by reversed-phase HPLC combined with solvent extraction. The molar absorptivity and chelate composition of Ni-FDO chelate were also determined. In addition, the linearity of calibration curves and the detection limit of the Ni ion were investigated. Effects of foreign ions on the determination of the Ni ion were also examined with 57 metal ions. The HPLC method was applied to determination of the Ni(II) ions in the spiked river water sample.

EXPERIMENTAL

Instrumentation

The HPLC system consisted of a Jasco PU-1580i inert pump (Japan Spectroscopic Co., Ltd, Tokyo, Japan), a Rheodyne 9725 inert injector (Cotati, CA) equipped with a 200 μL sample loop of polyether etherketone (PEEK), an SPD-10AV*VP* photometric detector (Shimadzu Co., Kyoto, Japan), a Cosmosil 5 C_{18} MS-II stainless steel column (150 × 4.6 mm ID, Nacalai Tesque, Kyoto, Japan), a Shimadzu Chromatopac C-R8A integrator, and a Thermo Minder SX-10R thermostat water bath (Taitec Co., Koshigaya, Japan). A longer Cosmosil 5 C_{18}-MS-II column (250 × 4.6 mm ID) was

also used for a screening test. All HPLC units were connected with the PEEK tubes. 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 Ni-FDO chelate. Micropipettes were used for a 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 agent α-furyl dioxime (FDO, β- and γ- form free) was obtained from Tokyo Kasei Kogyou Co. Ltd. (Tokyo, Japan). Further details are shown in Figure 1. The FDO was dissolved in 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK) in a concentration of 0.1 mol/L (M). The 0.1 M FDO was preserved in a refrigerator (about 4°C). Nitric acid (60%), acetic acid (99.9%), and ammonia water (25%) of super special grade for metal analysis were purchased from Wako Pure Chemical Industries (Osaka, Japan). A Ni standard of 1000 μg/mL (ppm) for AAS was obtained from Wako. The other Ni solutions were prepared by dilution of the above solution (1000 ppm) with 0.1 M HNO_3. The 58 metal standard solutions used are summarized in Table 1. Methanol was distilled and filtered through a membrane filter (pore size, 0.45 μm). Ammonia-ammonium chloride (NH_3–NH_4Cl) buffer solutions (pH 8.0–11.0) were prepared with 2 M ammonia and 2 M ammonium chloride solutions. Acetate buffer solutions (pH 4.0–7.0) were prepared with 2 M acetic acid and 2 M sodium acetate solutions. River water was collected from the Asano River (Kanazawa, Japan). The river water was filtered through a membrane filter (0.45 μm pore size), and the filtrate was used as the river 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 Ni standard

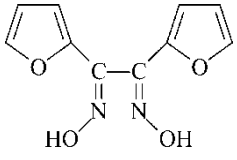

Figure 1. Structure of α-furyl dioxime (FDO). $C_{10}H_8N_2O_4 = 220.18$, CAS No. 23789-34-6.

Table 1. Metal standard solutions used (1000 ppm)

Metal	Salt	Medium	Metal	Salt	Medium
Ag(I)	$AgNO_3$	0.1 M HNO_3	Mo(VI)	$(NH_4)_6Mo_7O_{24}$	H_2O
Al(III)	$Al(NO_3)_3$	0.5 M HNO_3	Na(I)	NaCl	H_2O
As(III)	As_2O_3	NaOH in water pH 5 with HCl	Nb(V)	NbF_5	1 M HF
Au(III)	$HAuCl_4$	1 M HCl	Nd(III)	$Nd(NO_3)_3$	1 M HNO_3
Ba(II)	$BaCl_2$	1 M HCl	Ni(II)	$Ni(NO_3)_2$	0.1 M HNO_3
Be(II)[a]	$BeSO_4$	0.03 M HNO_3	Pb(II)	$Pb(NO_3)_2$	0.1 M HNO_3
Bi(III)	$Bi(NO_3)_3$	0.5 M HNO_3	Pd(II)	$PdCl_2$	1 M HCl
Ca(II)	$CaCO_3$	0.1 M HNO_3	Pr(III)	$Pr(NO_3)_3$	1 M HNO_3
Cd(II)	$Cd(NO_3)_2$	0.1 M HNO_3	Pt(IV)	H_2PtCl_6	1 M HCl
Ce(III)	$Ce(NO_3)_3$	1 M HNO_3	Rh(III)	$Rh(NO_3)_3$	2 M HNO_3
Co(II)	$Co(NO_3)_2$	0.1 M HNO_3	Sb(III)	$SbCl_3$	3 M HCl
Cr(VI)	$K_2Cr_2O_7$	0.1 M HNO_3	Sc(III)[a]	Sc (metal)	1 M HNO_3
Cs(I)	$CsNO_3$	0.5 M HNO_3	Se(IV)	SeO_2	0.1 M HNO_3
Cu(II)	$Cu(NO_3)_2$	0.1 M HNO_3	Si(IV)	Na_2SiO_3	0.2 M Na_2CO_3
Dy(III)	$Dy(NO_3)_3$	1 M HNO_3	Sm(III)	$Sm(NO_3)_3$	1 M HNO_3
Er(III)	$Er(NO_3)_3$	1 M HNO_3	Sn(II)	$SnCl_2$	6 M HCl
Eu(III)	$Eu(NO_3)_3$	1 M HNO_3	Sr(II)	$Sr(NO_3)_2$	1 M HNO_3
Fe(III)	$Fe(NO_3)_3$	0.1 M HNO_3	Ta(V)	TaF_5	1 M HF
Ga(III)	$Ga(NO_3)_3$	1 M HNO_3	Tb(III)	$Tb(NO_3)_3$	1 M HNO_3
Gd(III)	$Gd(NO_3)_3$	1 M HNO_3	Te(IV)	$TeCl_4$	6 M HCl
Ge(IV)	GeO_2	H_2O	Ti(IV)	$Ti(SO_4)_2$	1 M H_2SO_4
Hg(II)	$HgCl_2$	0.02 M HCl	Tl(I)	$TlNO_3$	1 M HNO_3
Ho(III)	$Ho(NO_3)_3$	1 M HNO_3	Tm(III)	$Tm(NO_3)_3$	1 M HNO_3
In(III)	In (metal)	0.5 M HNO_3	V(V)	NH_4VO_3	0.45 M H_2SO_4
K(I)	KCl	H_2O	W(VI)	Na_2WO_4	H_2O
La(III)	$La(NO_3)_3$	1 M HNO_3	Y(III)	$Y(NO_3)_3$	1 M HNO_3
Lu(III)	$Lu(NO_3)_3$	1 M HNO_3	Yb(III)	$Yb(NO_3)_3$	1 M HNO_3
Mg(II)	$Mg(NO_3)_2$	0.1 M HNO_3	Zn(II)	$Zn(NO_3)_2$	0.1 M HNO_3
Mn(II)	$Mn(NO_3)_2$	0.1 M HNO_3	Zr(IV)	$ZrO(NO_3)_2$	1 M HNO_3

[a]Concentrations of the Be(II) and Sc(III) ions were 100 ppm.

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 NH_3-NH_4Cl buffer solution (pH 9.0) to the centrifuge tube. After mixing the contents, add 700 μL of 0.1 M FDO/MIBK solution into the tube. Shake the contents for 10 minutes. After standing for 10 minutes, collect the organic layer. Determine the Ni concentration in the extract as Ni-FDO chelate under the following HPLC conditions. Column: Cosmosil 5 C_{18} MS-II (150 × 4.6 mm ID, particle size 5 μm), column temp.: 40°C, eluent: methanol/water (85:15, v/v), flow rate: 1.0 mL/min, injection volume of organic layer: 5 μL, detection wavelength: 435 nm.

Screening Test for 58 Metal Ions

A 25 μL aliquot of each metal solution of 1,000 ppm (Be, Sc: 100 ppm), 5 mL of water, 1 mL of 2 M NH_3-NH_4Cl buffer solution (pH 9.0), and 500 μL of 0.1 M FDO were added to a 10 mL centrifuge tube. After shaking for 20 minutes, the organic layer was separated and used for HPLC analysis. The HPLC conditions used were as follows: column, Cosmosil 5 C_{18}-MS-II (250 × 4.6 mm ID, 40°C); eluent, methanol/water/0.1 M FDO (79:20:1, v/v); detection, 430 nm; injection volume of organic layer, 5 μL. A blank test was also carried out, and the chromatographic peaks were compared.

Chelate Composition of Ni-FDO Chelate

A 2 mL of water, xμL of 1.70×10^2 M (1000 ppm) Ni standard solution, (400-x) μL of 0.1 M HNO_3, yμL of 1.00×10^2 M FDO, (2000-y) μL of MIBK, and 1 mL of 2 M NH_3-NH_4Cl buffer solution (pH 9.0) were added to a 10 mL centrifuge tube. After shaking for 20 minutes, each organic layer was chromatographed, and the peak area of the Ni-FDO chelate was measured. Here, (x, y) were (0, 680), (40, 612), (80, 544), (120, 476), (160, 408), (200, 340), (240, 272), (280, 204), (320, 136), (360, 68), and (400, 0). The mole fractions of [Ni]/([Ni] + [FDO]) were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively.

Visible Absorption Spectrum of Ni-FDO Chelate

A 2 mL of water, 500 μL of 8.52×10^5 M (5 ppm) Ni standard solution, 1000 μL of 2 M NH_3-NH_4Cl buffer solution (pH 9.0), 700 μL of 0.1 M FDO, and 2300 μL of MIBK were added to a 10 mL centrifuge tube. Two sample solutions were prepared, and the two organic layers were combined after shaking for 20 minutes. For a blank solution, 500 μL of 0.1 M HNO_3 was added instead of 500 μL of a 5 ppm Ni standard. The visible absorption spectrum of the Ni-FDO chelate was measured with the organic layers of standard and blank solutions.

Effect of Foreign Ions

The effect of foreign ions on the determination of the Ni ion was tested with 57 metal ions. Each foreign ion, 500 μL of 0.5 ppm Ni standard, and 500 μL of 0.1 M HNO_3 were placed into a centrifuge tube. Then, water was added up to the level of 5 mL (Ni concentration: 0.05 ppm). A 2 mL of 2 M NH_3-NH_4Cl buffer solution (pH 9.0) and 700 μL of 0.1 M FDO were added to the centrifuge tube. After extraction, the concentration of the Ni ion in the 5 mL

solution was determined by the recommended HPLC method. The recovery percentage was calculated from the peak area of the Ni chelate and that of the Ni standard (0.05 ppm) containing no foreign metal ion. 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 Ni(II) ion.

Recovery Test with a River Water Sample

As no Ni ion in the river water sample was detected by the HPLC method, the Ni ions were added to the river water sample. A 4.0 mL of a river water sample, 500 μL of Ni standard (5, 0.5, and 0.05 ppm), and 500 μL of 0.1 M HNO_3 were added to a centrifuge tube. In addition, 2 mL of 2 M NH_3-NH_4Cl buffer solution (pH 9.0) and 700 μL of 0.1 M FDO were added to each centrifuge tube. After shaking for 10 minutes, the Ni concentrations in these solutions (500, 50, and 5 ppb Ni) were determined according to the recommended procedure, and the recovery percentages were calculated.

RESULTS AND DISCUSSION

Extraction Conditions

Extraction pH and shaking time were investigated according to the recommended procedure. The effect of pH on extraction of the Ni-FDO chelate is shown in Figure 2. As constant peak areas were obtained over the pH range of 7.5 to 9.0, 2 mL of 2 M NH_3-NH_4Cl buffer solution of pH 9.0 was used in the recommended extraction procedure. When the buffer solution of pH 9 was used, the Ni(II) ion was quantitatively extracted into

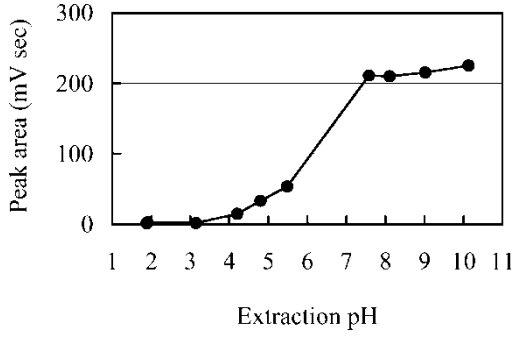

Figure 2. Effect of pH on extraction of Ni-FDO chelate. Buffer solutions used: 2 M CH_3COOH-CH_3COONa (pH 4.0, 5.0, 6.0, 7.0), 2 M NH_3-NH_4Cl (pH 8.0, 8.5, 9.0, 10.0, 11.0).

the MIBK by shaking for 5–60 minutes. Subsequently, 10 minutes was selected as the optimum shaking time.

The extracted Ni-FDO chelate in the MIBK solution was found stable for at least 7 hours, because the peak areas of the Ni chelate were almost constant. Thus, immediate injection of the organic layer was not required. Initially, 1 mL of 1 M NH_3-NH_4Cl buffer solution (pH 9.0) was added. However, the volume was changed to 2 mL in order to obtain a higher buffer capacity.

Separation Conditions and Injection Volume

The screening test for 58 metal ions indicated that gold (Au), cobalt (Co), copper, palladium (Pd), and Ni ions were extracted into the organic layer (MIBK) as yellow color chelates at pH 4–5. Among the ions, Au, Pd, and Ni chelate produced chromatographic peaks (430 nm detection). The extracted Au chelate eluted almost at the solvent front. On the other hand, the Pd chelate was found unstable in the MIBK because the color of the organic layer (yellow) decreased with time. When extraction was carried out at pH 8 (recommended procedure), the Co chelate eluted almost at the solvent front, while the Ni chelate eluted at a reasonable retention time. The other metal ions produced no chromatographic peak. The results indicated that a longer column (250 mm) was not required for selective determination of the Ni ion. Thus, a shorter column (150 × 4.6 mm ID) was employed for sensitive detection and rapid elution of the Ni-FDO chelate. Initially, the FDO was added to the eluent of methanol/water as a stabilizer for the Ni-FDO chelate. However, the Ni-FDO chelate was found stable in the absence of the FDO in the eluent. Considering the above results, the eluent of methanol/water (85:15, v/v) was employed.

Injection volume of the organic layer (MIBK) was also investigated in the range of 1–20 μL. The peak area of the Ni chelate was proportional to an injection volume in the range of 1–20 μL, while height was 1–5 μL. Thus, 5 μL was selected as the optimum injection volume of the organic layer.

Ni-FDO Chelate Composition

The composition of the Ni-FDO chelate was investigated by Job's method. The peak areas were plotted against the mole fractions of [Ni]/([Ni] + [FDO]). The results were not too good, as shown in Figure 3. Although, a clear maximum point could not be decided, probably due to low concentrations of Ni ion and FDO, the maximum point was estimated in the range of 0.31–0.36. Higher Ni ion and FDO concentrations resulted in the precipitation of Ni-FDO chelate due to low solubility in the MIBK. If the mole ratio of Ni:FDO is 1:2, the mole fraction of the maximum point

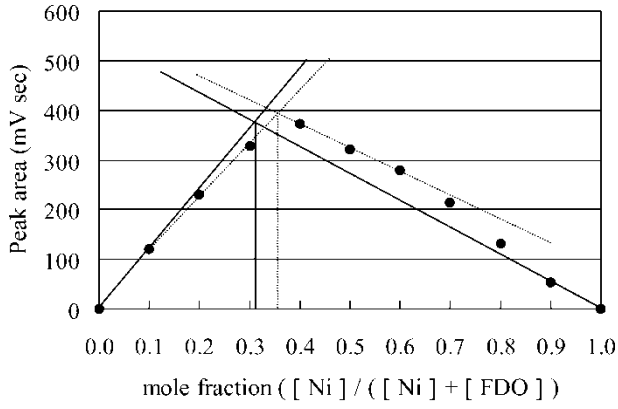

Figure 3. Determination of Ni-FDO chelate composition by Job's method. Experimental conditions are in the text.

must be 0.333. The mole fraction of 0.31–0.36 suggested that the mole ratio of Ni:FDO is probably 1:2.

Detection Wavelength and Molar Absorptivity of Ni-FDO Chelate

The visible absorption spectrum of the Ni-FDO chelate was measured, and is shown in Figure 4. For sensitive detection of the Ni-FDO chelate, the maximum absorption wavelength of 435 nm was selected. When the Ni ion was quantitatively extracted into 2.5 mL of the organic layer (MIBK), the concentration of Ni-FDO chelate was calculated as 1.42×10^{-5} M. Figure 4 shows that the absorbance at 435 nm is 0.24. Accordingly, the molar absorptivity of the Ni-FDO chelate was calculated as 1.7×10^4 from Lambert-Beer's Law ($0.24 = \varepsilon \times 1.42 \times 10^{-5}$ mol/L $\times$ 1 cm).

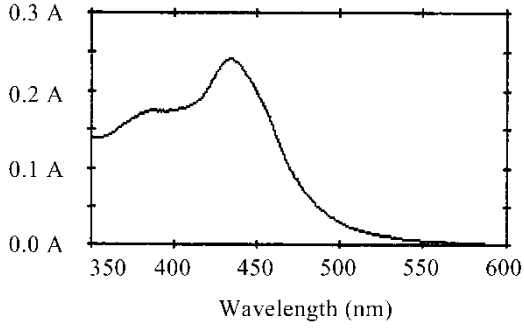

Figure 4. Visible spectrum (350–600 nm) of Ni-FDO chelate. Concentration of Ni-FDO chelate in MIBK was 1.42×10^{-5} M. A is absorbance. A: absorbance unit.

Calibration Curves, Repeatability, and Detection Limit

The calibration curves for Ni(II) ions were prepared with the Ni standards of varying concentrations by the recommended procedure. The correlation coefficients of the calibration curves obtained with 5 mL Ni standards were more than 0.999 over the range of 1 ppb to 1 ppm. Although, the correlation coefficients (CC) of the calibration curves varied day by day, the values of CC were more than 0.999. Further details are shown in Table 2.

Relative standard deviations of peak areas (N = 6) for 1 and 0.1 ppm Ni standards were less than 2%.

The detection limit of the Ni ion in 5 mL of water was estimated as 0.8 ppb, which corresponded to 3 times the standard deviation of the blank peak area.

Effect of Foreign Ions

The effect of 57 foreign ions on the determination of 0.05 ppm Ni(II) ion (5 mL) was investigated. Table 3 shows that 48 metal ions did not interfere,

Table 2. Calibration curves for Ni(II) ion and repeatability of peak areas

Concentration range	Equation of line	Correlation coefficient	Measuring point (ppb)
Calibration curves for Ni ion			
100–1000 ppb	$y = 0.3161x + 0.5552$	0.9999	0, 100, 200, 400, 600, 800, 1000
10–100 ppb	$y = 0.2978x + 1.4808$	0.9997	0, 10, 20, 40, 60, 80, 100
1–10 ppb	$y = 0.3026x + 0.8881$	0.9996	0, 1, 2, 4, 6, 8, 10

1 ppm Ni standard			0.1 ppm Ni standard		
No. of run	Peak area	Peak area	No. of run	Peak area	Peak area
Repeatability of peak areas (mV sec)					
1	346.391	365.496	1	48.901	50.172
2	346.791	365.375	2	51.336	50.259
3	355.675	367.165	3	50.566	50.064
4	351.981	368.219	4	50.541	50.453
5	352.777	363.582	5	50.557	50.609
6	357.538	352.336	6	50.540	51.424
Average	351.859	363.696	Average	50.407	50.497
SD[a]	4.544	5.790	SD[a]	0.802	0.495
RSD[b] (%)	1.3	1.6	RSD[b] (%)	1.6	1.0

y: peak area (mV sec), x: concentration of Ni ion (ppb).

[a]Standard deviation.

[b]Relative standard deviation.

Table 3. Effects of foreign metal ions on determination of 0.05 ppm Ni(II) ion

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

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 Ni(II) ion (0.05 ppm).

at 800 times or more, the concentration of the Ni ion. The Rh(III) ion of 1 ppm, 10 ppm Co(II) ion, and 10 ppm Sn(II) ion interfered with the determination of 0.05 ppm Ni ion. The Co(II) ion also extracted into the MIBK as Co-FDO chelate, and the chelate eluted almost at the solvent front. The interferences of Rh(III), Sb(III), Sn(II), and Te(IV) ions were partly due to the high concentration of hydrochloric or nitric acids in their 1000 ppm metal standards as shown in Table 1. Further details are shown in Table 3.

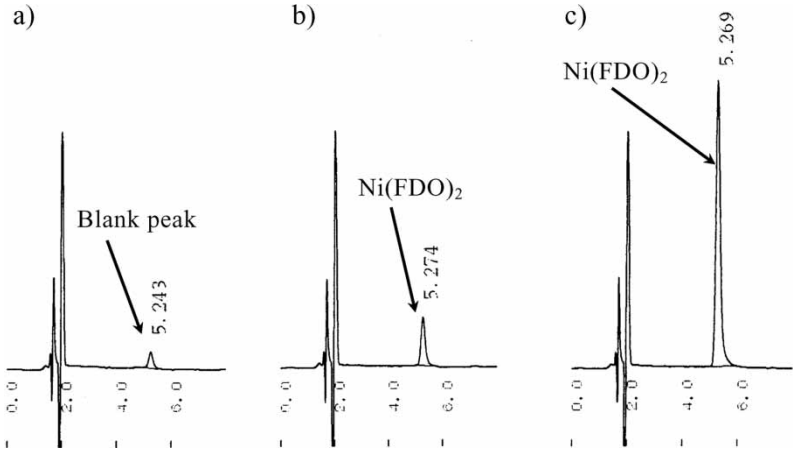

Figure 5. Chromatograms of blank and Ni-FDO chelates with Ni spiked river water sample. a) blank, b) 5 ppb Ni in 5 mL river water sample, c) 50 ppb Ni in 5 mL river water sample.

Recovery Tests of Ni Ion with a River Water Sample

Typical chromatograms of the Ni-FDO chelates are shown in Figure 5. The results of the recovery tests for 500, 50, and 5 ppb Ni ions are summarized in Table 4. The recoveries of 500, 50, and 5 ppb Ni ions were $100.5 \pm 1.5\%$, $101.2 \pm 1.5\%$, and $97.5 \pm 6.4\%$, respectively. The correlation coefficients of the calibration curves were more than 0.999. The high recoveries indicated that the ions in river water did not interfere with the proposed HPLC method for the Ni ion of ppb level.

CONCLUSION

In this study, a simple solvent extraction was carried out prior to HPLC analysis. Although, the concentration factor calculated from the volumes of

Table 4. Recovery tests for Ni ion with a river water sample

No. of run	Sample (ppb)	Added (ppb)	Found (ppb)	Recovery (%)	Equation of calibration curve	Correlation coefficient
500 ppb						
1	0	500	491.7	98.7	$y = 0.3276x + 1.6307$	0.9999
2	0	500	495.7	99.5		
3	0	500	500.0	100.4		
4	0	500	505.2	101.4		
5	0	500	510.7	102.5		
Av.			500.6	100.5		
SD			7.5	1.5		
RSD			1.5	1.5		
50 ppb						
1	0.0	50.0	47.76	98.9	$y = 0.3238x + 1.0591$	0.9999
2	0.0	50.0	48.55	100.5		
3	0.0	50.0	49.32	102.0		
4	0.0	50.0	49.59	102.6		
5	0.0	50.0	49.39	102.2		
Av.			48.92	101.2		
SD			0.76	1.5		
RSD			1.6	1.5		
5 ppb						
1	0.00	5.00	5.52	97.9	$y = 0.3026x + 0.8881$	0.9997
2	0.00	5.00	5.37	95.0		
3	0.00	5.00	6.03	108.2		
4	0.00	5.00	5.36	94.7		
5	0.00	5.00	5.19	91.5		
Av.			5.49	97.5		
SD			0.32	6.4		
RSD			5.8	6.6		

the sample solution (5 mL) and the organic layer (0.7 mL) was only about 7, the lower determination limit of the Ni ion in a 5 mL sample solution was 1 ppb, due to high molar absorptivity of the Ni-FDO chelate (1.4×10^4 at 435 nm). The FDO was found to be a selective and sensitive chelating agent for the Ni(II) ion compared with *o*-salicylideneaminophenol.[10] The presented method does not require chlorinated solvents and acetonitrile for extraction and HPLC separation. The HPLC analysis time is 8 minutes. The HPLC method was applied to the determination of the Ni ion in river water with precise results.

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