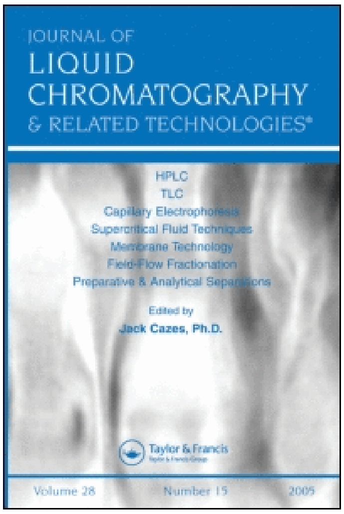

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SELECTIVE DETERMINATION OF NICKEL ION BY SOLVENT EXTRACTION AS *o*-SALICYLIDENEAMINOPHENOL CHELATE FOLLOWED BY LIGAND EXCHANGE AND REVERSED-PHASE HPLC WITH PHOTOMETRIC DETECTION

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ABSTRACT

Nickel ion was extracted into mixed solvents of 4-methyl-2-pentanone and 1-decanol (3 : 1, v/v) as *o*-salicylideneaminophenol (SAPH) chelate at pH 9. Organic layers of 5 μL and 10 μL of 10 mmol/L hexamethyleneammonium hexamethylenedithiocarbamate (HMA-HMDC) were injected into a C_{18} column. The Ni-SAPH chelate was converted to Ni-HMDC chelate on the column and detected at 325 nm. The correlation coefficient of the calibration curves obtained with 5 mL of nickel solution was more than 0.999 over the range of 10 ng/mL to 10 μg/mL. Recovery tests were carried out with snow samples

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and nickel standard solutions. The recoveries for 500 ng/mL and 50 ng/mL Ni ion were 105% and 95%, respectively. Linearity of the calibration curves and recovery were more excellent than those of ICP-AES. Effects of foreign ions on the method were investigated with 49 metal ions. Almost all ions did not interfere except for Rh(III) and Mn(II).

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 analysis of metal ions. ICP-AES and ICP-MS are expensive and not popular apparatuses. Detection sensitivity of AAS and ICP-AES differs 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 (1–3). The authors developed multi-element simultaneous determination methods by reversed-phase (RP) HPLC with photometric detection using dithiocarbamate (4–6) and β-diketones (7,8) as pre-column chelating reagents. In the case of photometric detection of a metal chelate, detection sensitivity is proportional to the molar absorptivity of each chelate. A more sensitive quantitative analysis is possible by combining pre-column derivatization HPLC with appropriate pre-concentration.

A lot of chelating reagents have been used to determine metal ions by molar absorption spectroscopy with or without solvent extraction, and some of the chelating reagents have been successfully utilized in RP-HPLC determination of metal ions. The chelating reagent *o*-salicylideneaminophenol (SAPH) has been used for determination of copper by molar absorption spectroscopy combined with solvent extraction (9), and for determination of aluminum (10) and beryllium (11) by spectrofluorimetry. However, metal chelates sometimes dissociate in reversed-phase eluents and give no peak. In our previous works, the chelating reagents were added to the eluents to prevent the on-column dissociation of metal chelates. However, the metal-SAPH chelates were still not stable even though the chelating reagent (SAPH) was added to the eluent.

In this paper, we propose a ligand exchange technique with hexamethyleneammonium hexamethylenedithiocarbamate (HMA-HMDC) for RP-HPLC metal analysis. Nickel ion was extracted into an organic layer as SAPH chelate, and the chelate was separated and determined as HMDC chelate on a C_{18} column with the eluent of methanol/water (containing no chelating reagent). This technique will improve the selectivity of the solvent extraction-HPLC method, and make it possible to use certain chelating reagents, which form unstable chelate in a reversed-phase eluent. In addition, the presented method does not use chlorinated solvents for extraction or HPLC separation.

EXPERIMENTAL

Instrumentation

The HPLC system consisted of a Jasco PU-1580i inert pump (Japan Spectroscopic Co., Ltd, Tokyo, Japan), Rheodyne 9125i injector (Cotati, CA), Jasco UVIDEC-100-VI photometric detector, Cosmosil 5 C_{18}-MS stainless steel column (250 × 4.6 mm i.d., Nacalai Tesque, Kyoto, Japan), Shimadzu Chromatopac C-R8A data processor (Shimadzu Co., Kyoto, Japan), and thermostat water bath (40°C). A micro syringe with stainless steel plunger was used for sample injection. A Yamato SA-31 auto-shaker (Yamato Scientific Co., Ltd., Tokyo, Japan) was used for solvent extraction. A Plasma-Spec I ICP-AES (Leeman Labs Inc., MA) was also used for Ni analysis.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated. Milli-Q water was used for aqueous solution preparation. The chelating reagent SAPH (CAS No. 1761-56-4) was obtained from Dojindo Laboratories (Kumamoto, Japan) for use as a 4-methyl-2-pentanone (MIBK) solution (2 mmol/L). Nickel standard solution of 1000 µg/mL (ppm) for AAS was obtained from Wako Pure Chemical Industries (Osaka, Japan). The solution was prepared with $Ni(NO_3)_2$ and 0.1 mol/L HNO_3. The other Ni solution was obtained by dilution of the above solution (1000 ppm) with Milli-Q water and adjusted to pH 1 with hydrochloric acid. Methanol was distilled and filtered through a membrane filter (pore size, 0.45 µm). Ammonia solution of 1 mol/L was prepared by dilution of 25% ammonia solution of special grade for metal analysis (Wako) with Milli-Q water. Ammonia–ammonium chloride (NH_3–NH_4Cl) buffer solution was prepared with 1 mol/L ammonia solution and 1 mol/L ammonium chloride. HMA-HMDC was synthesized according to the previous work (4), and dissolved with Milli-Q water to the required concentration. Snow samples were collected at Hokuriku University. The snow was melted by a water bath then filtered through a membrane filter (0.45 µm pore size). Eluent compositions were expressed as volume ratios.

Extraction Conditions

In order to determine Ni ion by RP-HPLC, a chelation step with SAPH is required. We employed solvent extraction for the chelation and concentration of Ni ion. To a 10 mL centrifugation tube with plug, 5 mL of Ni standard solution (0.5 ppm) and 1 mol/L ammonia solution were added until a light red color was obtained. Then, exactly 0.5 mL of NH_3–NH_4Cl buffer solution of various pH, 0.3 mL of 2 mmol/L SAPH MIBK solution, and 0.1 mL of 1-decanol were added. The content was shaken for 10 min, and a 5 μL aliquot of the organic layer was injected with 20 μL of 10 mmol/L HMA-HMDC into a C_{18} column. The peak areas of Ni-chelate were plotted against the pH of the aqueous layer to select optimum extraction pH.

Optimum shaking time was investigated in a similar manner with three Ni solutions (5 ppm, 0.5 ppm, and 0.05 ppm).

The effect of SAPH concentration on an extract of Ni ion was also examined over the range from 1 to 10 mmol/L.

HPLC Conditions

HMA-HMDC was injected with the SAPH chelate because Ni-SAPH chelate is unstable in a reversed-phase eluent such as methanol/water. The chelate could be converted to stable HMDC chelate on the column and detected at 325 nm, which is the maximum absorption of the Ni-HMDC chelate. Thus, the effect of the amount of HMA-HMDC on ligand exchange reaction was studied with 10 mmol/L HMA-HMDC. Methanol-water eluent was used for elution of the chelate. The column temperature was set at 40°C by considering the column pressure.

The effect of the injection volume on the peak shape of Ni chelate was also examined.

Calibration Curves of Ni Ion

To investigate the linear range of the calibration curve of Ni ion, calibration curves were prepared with metal solutions of varying concentrations by the recommended procedure. Correlation coefficients and equations of the calibration curves (0.01–0.1 ppm, 0.1–1.0 ppm, 1–10 ppm) were computed.

Reproducibility and Detection Limit

According to the recommended procedure, six standard solutions of 5 ppm Ni were analyzed. Relative standard deviations (RSD) of peak areas were calculated. Similar experiments were carried out for 0.5 ppm and 0.05 ppm solutions.

The standard deviation (SD) of blank peak areas was obtained by 10 replicated blank tests. Detection limits of Ni (ng/mL) were calculated by 3SD and peak area of 50 ng/mL Ni standard.

Effect of Foreign Ions

The effects of foreign ions on the determination of Ni were tested with 49 metal ions. Each foreign ion and 0.5 mL of 5 ppm Ni standard were taken into a centrifuge tube, and diluted to 5 mL with Milli-Q water. The solution was analyzed by the recommended procedure and the peak area was measured. The recovery percentage was calculated from the peak area and that of Ni standard solution containing no foreign metal ions.

Recovery Test with a Snow Sample

Collected snow was taken into a 1 L beaker and heated in a water bath to melt it. The solution was then filtered through a membrane filter (pore size, 0.45 μm). The resultant solution of 4 mL was taken into a centrifuge tube and 1 mL of Milli-Q water was added. One milliliter of Ni solution was also added to the 4 mL snow sample. Nickel concentrations in these solutions were determined by the presented method, and the recovery % was calculated by the results. A similar experiment was carried out by ICP-AES (Ar plasma, 40 MHz) with 221.65 nm for detection of Ni.

RESULTS AND DISCUSSION

Extraction Conditions

The higher the SAPH concentration, the larger the blank peak area. Thus, 2 mmol/L was selected to extract up to 10 ppm Ni ion in 5 mL solution. For shorter standing time, 1-dacanol was added with SAPH MIBK solution.

The effect of pH on extraction of Ni is shown in Figure 1. Figure 1 shows that Ni ion was quantitatively extracted at pH 8.0–9.5. Thus, NH_3–NH_4Cl buffer solution (pH 9) was employed for pH adjustment. When the pH 9 buffer solution was used, the pH of the aqueous layer was 8.66.

Effects of shaking times on extraction of Ni in 5 ppm, 0.5 ppm, and 0.05 ppm solutions were also investigated at pH 8.66. It was found that a constant

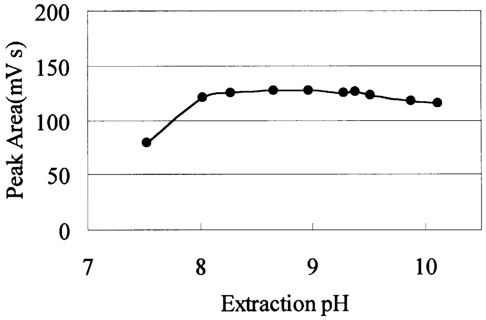

Figure 1. Effect of pH on extraction of Ni ion. Extraction conditions are the same as the recommended extraction procedure except for pH.

peak area was obtained at a shaking time of 5–40 min. Therefore, 10 min was used for the remainder of the work.

Recommended Extraction Procedure for Determination of Ni Ion

Transfer a sample or standard solution (5 mL) into a 10 mL centrifuge tube. Add 1 drop of 0.1% phenolphthalein solution. Titrate with 1 mol/L ammonia solution until a light red color is obtained. Add 0.5 mL of 1 mol/L NH_3–NH_4Cl buffer solution (pH 9), 0.3 mL of 2 mmol/L SAPH (MIBK solution), and 0.1 mL of 1-decanol. Shake the contents for 10 min. After standing for 5 min, inject 5 µL of the organic layer and 20 µL of 10 mmol/L HMA-HMDC into a C_{18} column.

HPLC Conditions

Composition of the methanol/water in the eluent is not so important because SAPH is a selective chelating agent for Ni ion and almost all metal ions gave no peak. Thus, a mixture of methanol/water (87 : 13, v/v) was used as an eluent and run at a flow rate of 1.2 mL/min. However, the amount of HMA-HMDC is important for ligand exchange reaction. The effects of 10 mmol/L HMA-HMDC amounts on ligand exchange of Ni-SAPH chelate to Ni-HMDC chelates were examined over the range from 1 to 100 µL with 5 mL of 10 ppm and 1 ppm Ni solutions. At first a sample solution (containing Ni-SAPH chelate) must be injected into the column, and then HMA-HMDC solution should be injected immediately for effective ligand exchange. Constant peak areas were obtained by addition of 10 µL or more of 10 mmol/L HMA-HMDC. Because excess amounts

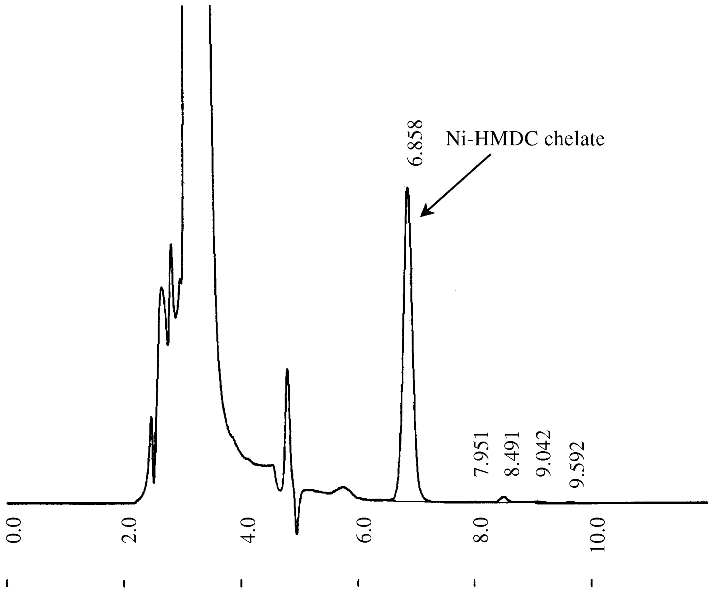

Figure 2. Typical chromatogram of Ni chelate. Column: Cosmosil 5 C_{18}-MS (250 × 4.6 mm i.d.), Column Temperature: 40°C, Eluent: methanol/water (87 : 13, v/v), Flow Rate: 1.2 mL/min, Detection Wavelength: 315 nm, Detection Sensitivity: 0.04 AUFS, Ni concentration in 5 mL solution: 0.2 μg/mL, Injection volume of sample: 5 μL, Injection volume of 10 mmol/L HMA-HMDC: 20 μL. Extraction conditions are the same as the recommended extraction procedure.

(40 μL or more) of HMA-HMDC resulted in a tailed peak of Ni chelate, 20 μL was employed.

The effect of the injection volume on the Ni-chelate peak and blank peak was also investigated over the range from 1 to 10 μL. An injection volume of 5 μL was employed because the peak area ratio of the standard to the blank was the highest. A micro syringe with a stainless steel plunger was used because a Ni-Ti alloy plunger gave a higher blank peak. A typical chromatogram is shown in Figure 2 with HPLC conditions.

Calibration Curves of Ni Ion

Calibration curves were obtained with three standard series according to the optimized conditions. The calibration curves have good linearity in the wide concentration ranges (0.01–10 μg/mL) as shown in Table 1.

Table 1. Calibration Curves of Ni Ion

Concentration Range	Equation of Line	Correlation Coefficient	Measuring Point (ppm)
1–10 ppm	$y = 248.09x + 5.6881$	0.99995	0, 1, 2, 4, 6, 8, 10
0.1–1 ppm	$y = 248.46x + 2.7465$	0.99990	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1 ppm	$y = 247.17x + 2.8099$	0.99960	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10

Table 2. Reproducibility of the Presented Method

Concentration of Ni	Mean Peak Area (mV s)	Standard Deviation	RSD%	No. of Run
5 ppm	1234.080	9.887	0.80	6
0.5 ppm	129.229	0.543	0.42	6
0.05 ppm	14.403	0.355	2.46	6

Table 3. Effects of Foreign Ions on Determination of 0.5 ppm Ni Ion

Tolerance Limit	Metal Ion
0.5 ppm	Rh(III)
1 ppm	Mn(II)
5 ppm	Co(II), Sn(II)
10 ppm	Cr(VI), Fe(III), Zn(II)
20 ppm	Al(III), Cu(II), Eu(III), Ga(III), Gd(III), Pd(II), Ru(III), Y(III), Nd(III)
50 ppm	Cd(II), Pr(III), Pt(IV), Sc(II), Te(IV), Tm(III), V(V),
100 ppm	Hg(II), Se(IV), Be(II), Bi(III), Ca(II), Dy(III), Er(III), Ho(III), Ge(IV), Sm(III), Tb(III), Ti(IV), Tl(I), W(VI), Yb(III), Zr(IV), In(III), K(I), La(III), Lu(III), Mg(II), Mo(VI), Pb(II), As(III), Au(III), Ba(II)

Table 4. Recovery Test with a Snow Sample

HPLC					ICP-AES				
Sample (ppm)	Added (ppm)	Found (ppm)	Recovery ± RSD(%)		Sample (ppm)	Added (ppm)	Found (ppm)	Recovery ± RSD(%)	
0.000	0.5	0.524	104.8 ± 1.0	N = 4	0.00	0.5	0.472	94.4 ± 3.0	N = 6
− 0.001	0.05	0.0466	95 ± 2	N = 4		0.05	not detected		

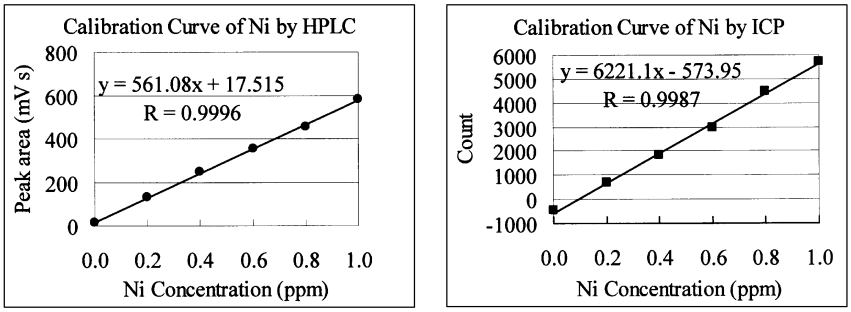

Figure 3. Calibration curves of Ni obtained by the presented HPLC method and ICP-AES. HPLC conditions are the same as in Figure 2 except for the detector range (0.02 AUFS).

Reproducibility and Detection Limit

Table 2 shows reproducibility of the method. The RSDs of the Ni-chelate peak areas at 5 ppm, 0.5 ppm, and 0.05 ppm were 0.80%, 0.42%, and 2.5%, respectively. The detection limit of Ni ion in 5 mL solution was 1 ng/mL, which corresponded to 3 times the standard deviation of the blank peak area.

Effects of Foreign Ions

The effects of foreign ions on the determination of Ni are shown in Table 3. The limiting value of the foreign ion concentration was taken as the value, which caused an error of more than 5% in the recovery of Ni ion. Although Rh (III) and Mn (II) interfered, the other metal ions could coexist at ten times or more the concentration of Ni ion.

Recovery Test with Snow Sample

Nickel concentration in snow solution was lower than the lower limit of determination (0.01 ppm). Thus, nickel standard solutions were added to snow solution at 0.5 ppm, and 0.05 ppm. Then the solutions were analyzed by the proposed method and ICP-AES. The results were summarized in Table 4. In the concentration range, the background noise of ICP-AES was larger than that of HPLC. Calibration curves by HPLC were better than those of ICP-AES (Figure 3). Though both recovery tests for 0.5 ppm Ni solution were good, the correlation coefficient of the calibration curve and lower detection limits were superior to those of ICP-AES.

CONCLUSION

Many chelating reagents have been used to determine metal ions by solvent extraction followed by molecular absorption spectroscopy. However, the formed metal chelate is often dissociated in the HPLC column, and could not be determined. Such a chelating reagent, which forms unstable chelate in eluent, cannot be utilized for HPLC analysis, even if the reagent has excellent selectivity for a certain metal ion. On the other hand, an unselective chelating reagent also has some disadvantages because of its difficulty of chelate separation and interference by other metal ions. The ligand exchange technique presented here will solve such problems.

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