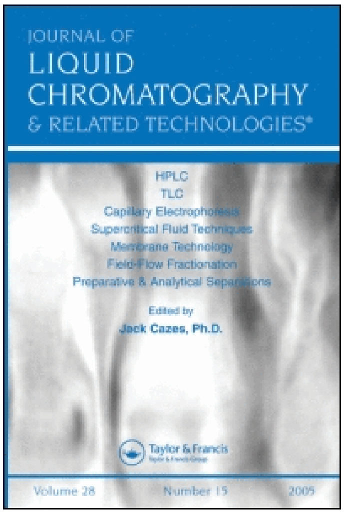

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Simultaneous Determination of Heavy Metals in Water by High Performance Liquid Chromatography after Solvent Extraction of Heavy Metals as Hexamethylenedithiocarbamato Chelates

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SIMULTANEOUS DETERMINATION OF HEAVY METALS IN WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AFTER SOLVENT EXTRACTION OF HEAVY METALS AS HEXAMETHYLENEDITHIOCARBAMATO CHELATES

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ABSTRACT

A simple, rapid, precise and accurate method for the simultaneous determination of ppb levels of cadmium(II), nickel(II), cobalt(II), copper(II), bismuth(III) and mercury(II) in water was developed. The six heavy metals described above in 50 ml of water sample were quantitatively extracted into 1.0 ml of chloroform by shaking for 15 min as their hexamethylenedithiocarbamato chelates (HMDC chelates), then separated by reversed-phase high performance liquid chromatography (HPLC) and the eluted metal chelates were monitored at 260 nm. The six HMDC-metal chelates were successfully separated on a 5 μm ODS column (4.6× 150 mm, Cosmosil 5 C_{18}), using methyl alcohol-water-diethyl ether-buffer solution (NH_4Cl-NH_3, pH 7.5)-10^{-3}M hexamethyleneammonium hexamethylenedithiocarbamate (HMA-HMDC)=82:9:3:3:3 as the eluent. The linear working curves for the six metals were obtained in the concentration range of 0.3-2000 ng/ml (ppb). Detection limits were 45-600 pg as metals. The recovery and the precision of the proposed method were examined for the composite sample containing the above metals and sixteen foreign ions, and these results were 99.2-101.5 % and 0.5-1.2 %, respectively. The proposed method was applied to the determination of the above six metals in river water and satisfactory results were obtained, compared with those by the flameless atomic absorption (FL-AAS) method.

INTRODUCTION

In recent years, HPLC has become of interest for the simple determination method for metals. HPLC method does not require

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expensive apparatus and skillfulness, and enables simultaneous determination of metals as comparable to FL-AAS or AAS method. N-substituted dithiocarbamates were frequently used as the chelating agent (1-7). Smith et al. (1) reported a simple method for the determination of nickel, cobalt, ion (III) and copper by HPLC using diethyldithiocarbamate (DDTC) as chelating agent. Their method required no pretreatment of sample water, but the detection limits and the reproducibility were not satisfactory (31 ppb and 11.6 %, respectively). Edward-Inatimi et al. (3) also reported HPLC analysis of metal ions after solvent extraction as DDTC chelates. But satisfactory detection limits and reproducibility were not obtained (50 ppb and 4 %, respectively). Young-Tung et al. reported sensitive HPLC method using n-butyl-2-naphthylmethyldithiocarbamate. This method, however, required time-consuming pretreatment (4 h) and large sample size (1000 ml) to analyze ppb levels of metals. Cassidy et al. (8-11) reported determination of ng/ml and pg/ml levels of metals in water or alloy by trace enrichment and HPLC. Their method employed gradient elution and postcolumn reaction. A gradient elution system is essentially inadequate for a routine analysis, because in general the reproducibility is not satisfactory for precise and accurate determination, and then the regeneration of column (time-consuming) and relatively expensive apparatuses are required.

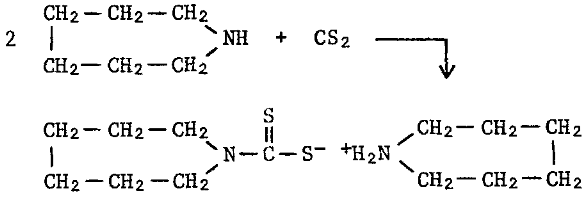
We have reported a simple and rapid method for the simultaneous determination of lead(II), nickel(II), cobalt(II), copper (II), mercury(II) and bismuth(III) in water after solvent extraction as their pyrrolidinedithiocarbamato chelates (APDC chelates) in the concentration range of 4-1000 ppb (6) and applied also to the simultaneous determination of lead(II), nickel(II) and copper (II) in Orchard Leaves (NBS, SRM 1571) (7).

In this paper, we describe a more sensitive method compared with the previous work (6) by using HMA-HMDC as chelating agent. The presented method was possible to determination cadmium (II) which could not determined by previous work (6).

MATERIALS

Reagents

All chemicals used were of analitycal grade purity unless otherwise stated. HMA-HMDC was prepared easily by the method described by Busev et al. (12), and recrystallized twice from methyl alcohol-diethyl ether (2:1). The final crystal was identified by elemental analysis and mass spectrometry. The symthetic method was summarised in the synthetic reaction (eq. 1). The crystal was preserved in glass bottles and stored at -15°C in a refrigerator. The HMA-HMDC solution of 10^{-2} M (for extraction) and 10^{-3} M (for eluent) were adjusted to pH 9.0 by addition of ammonium chloride-ammonia water buffer solution and preserved in polyethylene bottles and stored a refrigerator (5°C). The standard metal solutions were prepared as follows : each of the high-purity metals, such as cadmium, nickel, cobalt, copper and zinc, was dissolved in dilute super special grade hydrochloric or nitric acid, and the other metal solutions were prepared from the metal salts by dissolution with distilled water or slightly acidic or alkaline solution. Each stock solution was made up to contain the metal at a concentration of 1000 ppm. Each 50 ppm standard solution prepared by dilution of the stock solution was acidified to pH 1. A mixed standard solution (for preparation of working curves etc.) containing the six heavy metals (Cd:0.3 ppm, Ni:1.0 ppm, Co:0.5 ppm, Cu:1.0 ppm, Bi:1.0 ppm, Hg:2.0 ppm) were also adjusted to pH 1 with hydrochloric acid. One molar ammonium citrate, dibasic solution was prepared as follows : a 226 g (1 mol) of ammonium citrate, dibasic was dissolved with ca. 900 ml of distilled water then adjusted pH to 9.3 and added water up to 1000 ml. This solution was shaked with 0.01 % diphenylthiocarbazone-chloroform solution for three times in order to remove heavy metals. Two molar ammonium chloride-ammonia water buffer solution was prepared as follows : a 107 g (2 mol) of ammonium chloride was dissolved with ca. 900 ml of distilled water then adjusted to pH 9.0 with ammonia water and



EQUATION 1 Synthesis of Hexamethyleneammonium Hexamethylenedithiocarbamate (HMA-HMDC)

diluted with water up to 1000 ml. The heavy metals in the buffer solution used for the preparation of HMA-HMDC solution were also removed in the manner described above. Chloroform used was purified by distillation before use. The chromatographic solvents were prepared as follows : each commercial reagent-grade methyl alcohol and diethyl ether was distilled and filtered through a membrane filter (Toyo Roshi, TM-2P, 0.45 μ) ; distilled and deionized water was also filtered a membrane filter (Toyo Roshi, TM-2, 0.45 μ). Hydrochloric, nitric acid and ammonia water were super special grade commercial materials and used without further purification.

Apparatus

A liquid chromatograph consisting of a Model 6000 A pump (Waters Assoc.), a U6K universal injector (Waters Assoc.) and UVIDEC-100-III ultraviolet spectrophotometer (Japan Spectroscopic Co., Tokyo, Japan) was used. A 4.6×150 mm reversed-phase column (Cosmosil 5 C_{18} packed column, 5 μm, Nakarai Chemicals, Kyoto, Japan) was employed. This column was cooled at 10.0 ± 0.1°C by a Taiyo Scientific Industrial Co. Ltd. Model 150 L coolpipe and a Model Ace-80 thermominder in all runs. A Hitachi Model 200-20 spectrophotometer was employed for the measurment of UV spectra of HMDC-metal chelates. A Yamato Model SA-31 auto shaker was used for extraction of HMDC chelates and operated at a rate of ca. 250

r.p.m. in all experiments. FL-AAS analysis was performed by Nippon Jarrell Ash (Kyoto, Japan) Model AA-8500 atomic absorption, flame emission spectrometer equipped with Model FLA-100 flameless atomizer and Model MC-100 microprocessor concentration readout system.

METHODS

HPLC System

In general, dithiocarbamates and their metal chelates were thermodynamically unstable. The eluent, therefore, contained trace amount of HMA-HMDC, and the resevoir was cooled in an ice bath, and the column was adjusted to 20 ± 0.1°C. The bubbles which appeared in the connecting tube between a pump and a eluent reservoir by changing of eluent temperature (0°C → ca.20°C) were trapped with a glass tube (6 mm i.d. × 30 mm). Schematic diagram of the chromatographic system is shown in Fig. 1.

HPLC Separation of HMDC-Metal Chelates

A normal-phase (silica gel) and a reversed-phase (ODS) columns were examined as the stational phase, and verious solvents, such as n-hexane, cyclohexane, chloroform, iso-propylalcohol, methyl alcohol, acetonitrile, water, ethyl acetate, diethyl ether, ethyl alcohol etc., and their mixture were examined as the eluent.

Addition of 1.0×10^{-3} M HMA-HMDC to the eluent was needed for the reproducible chromatograms. In order to decide the optimum concentration of HMA-HMDC, the measurements of peak heights of HMDC chelates were carried out at verious HMA-HMDC concentrations.

The effect of injection volume of chloroform extract on the HPLC separation was also investigated.

Ultraviolet spectra of HMDC-metal chelates were measured to decide the detection wavelength.

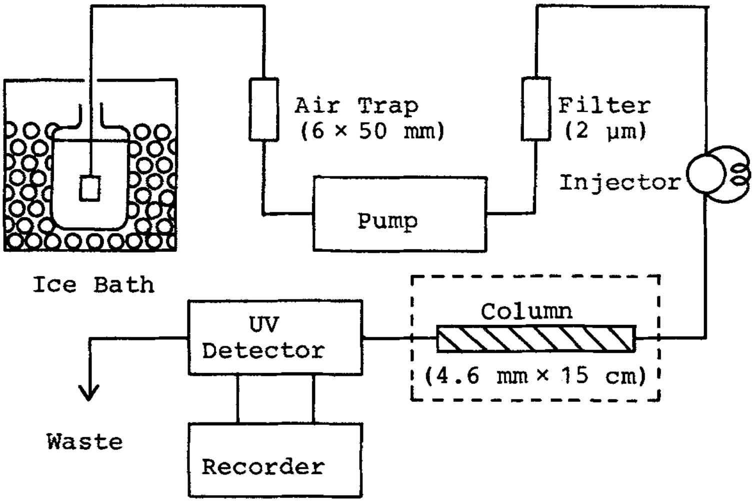


FIGURE 1 Schematic Diagram of the HPLC System.

Extraction Conditions

Optimum amount of HMA-HMDC and shaking time required for simultaneous quantitative extraction of the six heavy metals were investigated. The peak heights were measured at verious amount of HMA-HMDC solution and shaking time. The condition of extraction pH and the amount of buffer and masking agent solution for ion(III) were based on the previous work (6).

Working Curves

The working curves for the determination of six metals were prepared from 50 ml of standard solution containing the six metals, according to the recommended analytical procedure.

Recovery of the Metal Ions from Composite Sample

The effect of foreign ions coexisted on the determination of the six metals were investigated. The composite sample coexisting sixteen foreign ions was analysed by using the proposed method. The recovery and coefficient of variation for the determination of cadmium(II), nickel(II), cobalt(II), copper(II), bismuth(III) and mercury(II) were investigated.

Determination of Trace Amount of Metals in River Water

The proposed method was applied to the determination of metals in river water samples. The samples were taken from Tamatani, Gôtani and Kakehashi river (Komatsu, Japan), and they were adjusted to pH 1 with hydrochloric acid in situ, then they were stored in polyethylene bottles. After the samples were filtered through membrane filters (Toyo Roshi TM-2, 0.45 μ), the analysis were carried out for the filtrates by the proposed HPLC method and the FL-AAS method.

RESULTS AND DISCUSSION

HPLC Separation of HMDC-Metal Chelates

When reversed-phase column (cosmosil 5 C_{18}) and a mixed solution of methyl alcohol-water-diethyl ether-1.0×10^{-3} M HMA-HMDC were used, Cd(II)-, Ni(II)-, Co(II)-, Cu(II)-, Bi(III)- and Hg(II)-HMDC chelates were sufficiently separated. Addition of a buffer solution (NH_4Cl-NH_3, pH 7.5) to the eluent provided reproducible chromatograms. Decomposition rate of HMA-HMDC and HMDC chelates in the eluent are slow at a high pH, but the ODS columns can not use at more than pH 8. Thus the eluent was adjusted to pH 7.5. The peak heights of the chelates were reproducible in the HMA-HMDC concentration range of $2-6\times10^{-5}$ M.

When 5 μl or above chloroform extract was injected into the column, the width of each peak became broad, therefore 3.0 μl of chloroform extract was used in the HPLC procedure. A typical chromatogram and the optimum separation conditions were shown in Fig.2.

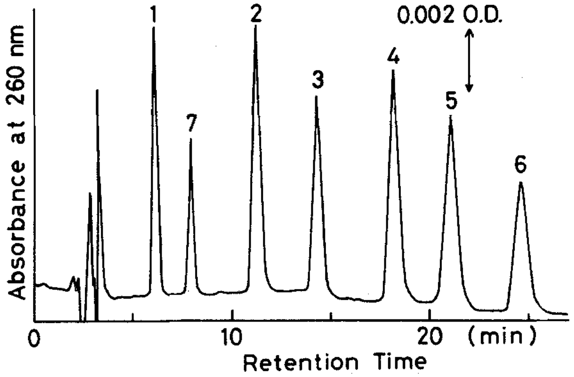


FIGURE 2 Typical Chromatogram of Standard HMDC Chelates

1 : Cd(2.3 ng), 2 : Ni(7.5 ng), 3 : Co(3.8 ng)
4 : Cu(7.5 ng), 5 : Bi(7.5 ng), 6 : Hg(15 ng)
7 : decomposition product of HMA-HMDC
HPLC conditions
Column : Cosmosil 5 C_{18} , 4.6 mm i.d. × 15 cm(10±0.1°C)
Eluent : methyl alcohol/water/diethyl ether/10^{-3} M HMA-HMDC/buffer solution(pH 7.5) = 82/9/3/3/3
Flow Rate : 0.8 ml/min, Injection Volume : 3.0 µl
Eluent reservoir was cooled in an ice bath.

Extraction Conditions

When 0.8 - 4.0 ml of 0.010 M HMA-HMDC was added, reproducible peak heights were obtained over the metal concentration range of 10 - 2000 ppb. The shaking time was investigated in the presence of 3.0 ml of 0.010 M HMA-HMDC over the range of 1 - 30 min. A part of the results was summarized in Fig. 3. The six heavy metals were quantitatively extracted by shaking for 10 - 20 min in the metal concentration range of 10 - 2000 ppb in the presence of 3.0 ml of 0.010 M HMA-HMDC. In the recommended procedure, 3.0 ml of 0.010 M HMA-HMDC and 15 min for shaking time were employed.

Recommended Analytical Procedure

From the studies described above, the following procedure is recommended for the simultaneous determination of cadmium(II),

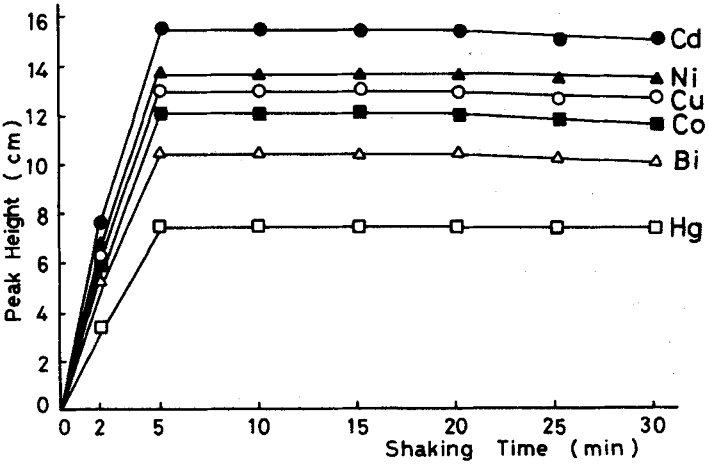


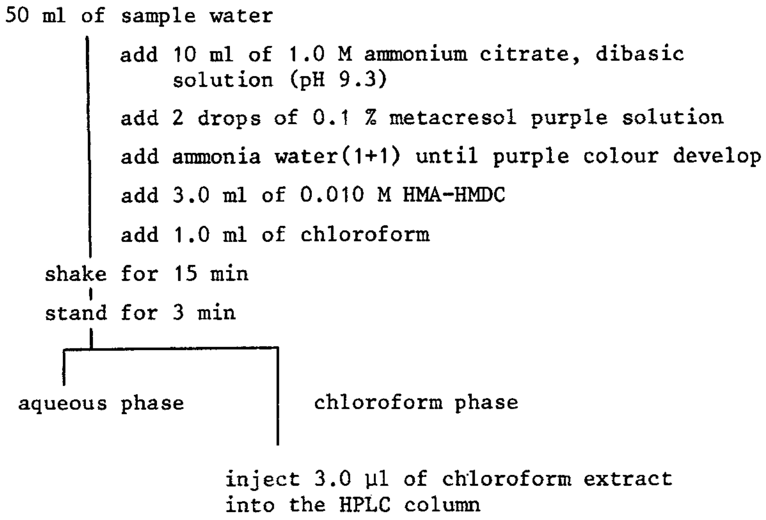
FIGURE 3 Effect of Shaking Time on the Extraction

Metal Concentrations
Cd : 30 ppb, Co : 50 ppb, Hg : 200 ppb, Ni,Cu,Bi : 100 ppb (detector range : 0.04 O.D.)
Extraction was carried out in the manner shown in Scheme 1.
HPLC conditions were same as shown in fig.2.

nickel(II), cobalt(II), copper(II), bismuth(III) and mercury(II) in water (Scheme 1) : a 50 ml of sample water containig 0.015 - 100 μg of each metal is put into a separatory funnel. Then the six heavy metals are extracted according to the recommended analytical procedure as shown in Scheme 1. A 3.0 μl portion of the chloroform extract was injected into the column (Cosmosil 5 C_{18} , 4.6 mm× 15 cm) which adjusted to 10.0 ± 0.1°C. The eluent (methyl alcohol - water - diethyl ether - buffer solution(pH 7.5) - 1.0×10^{-3} M HMA-HMDC = 82:9:3:3:3) cooled in an ice bath was flowed at a rate of 0.8 ml/min and the eluted HMDC-metal chelates were detected at 260 nm. The each amount of metal could be determined by measuring the peak height or the peak area.

Working Curves and Detection Limits

The working curves for the determination of the six metals were prepared with 50 ml of standard solution containing these six metals



SCHEME 1 Recommended Extraction Procedure for the Determination of Cd, Ni, Co, Cu, Bi and Hg by HPLC

according to the above procedure. All the working curves obtained showed good straight lines and passed through the origin. They were expressed by least-squares fitting. The regression lines obtained and values of correlation coefficient were summarized in Table 1.

Detection limits of each metal was 45 pg for cadmiun(II), 150 pg for nickel(II), 75 pg for cobalt(II), 150 pg for copper(II), 150 pg for bismuth(III) and 300 pg for mercury(II).

Recovery of Metal Ions from Composite Sample

The effects of presence of other ions on the determination of the six metals were investigated. The results were summarized in Table 2. The limiting value of the foreign ions was taken as that value which caused an error of less than 10 % in the recovery of each at least one metal. Lead(II) and zinc(II) influenced the recovery of nickel only, but almost ions did not have significant influence on the recovery of the six metal ions.

Table 1 Regression Lines of the Working Curves for the Six Heavy Metal Ions

	Metal Ion	Concentration Range (ppb)	Regression Line	Correlation Coefficient
(a)	Cd(II)	30 - 300	y*= 0.50843 x**	0.99985
	Ni(II)	100 - 1000	y = 0.15528 x	0.99967
	Co(II)	50 - 500	y = 0.31130 x	0.99970
	Cu(II)	100 - 1000	y = 0.17996 x	0.99972
	Bi(III)	100 - 1000	y = 0.14309 x	0.99899
	Hg(II)	200 - 2000	y = 0.05077 x	0.99821
(b)	Cd(II)	3 - 30	y = 0.59710 x	0.99948
	Ni(II)	10 - 100	y = 0.15297 x	0.99913
	Co(II)	5 - 50	y = 0.27304 x	0.99927
	Cu(II)	10 - 100	y = 0.15910 x	0.99864
	Bi(III)	10 - 100	y = 0.13045 x	0.99971
	Hg(II)	20 - 200	y = 0.04433 x	0.99959
(c)	Cd(II)	0.3 - 3.0	y = 0.81141 x	0.99917
	Ni(II)	1.0 - 10	y = 0.25629 x	0.99196
	Co(II)	0.5 - 5.0	y = 0.24250 x	0.99923
	Cu(II)	1.0 - 10	y = 0.11839 x	0.99920
	Bi(III)	1.0 - 10	y = 0.09932 x	0.99916
	Hg(II)	2.0 - 20	y = 0.03178 x	0.99839

Detector Range : (a);0.32 O.D., (b);0.04 O.D., (c);0.005 O.D. and all peak heights were calculated at 0.04 O.D.

y* : peak height at 0.04 O.D.(cm)

x** : metal concentration (ppb)

Table 2 Effect of Foreign Ions and Salts on the Determination of the six heavy metals*

Ion	Tolerance Limits	Ion or Salt	Tolerance Limits
Ag(I)	1.0 ppm	Sr(II)	500 ppm
As(III)	100 ppm	Pb(II)	0.05 ppm
Ca(II)	500 ppm	Zn(II)	0.1 ppm
Cr(III)	10 ppm	NaCl	1.0 %
Cr(VI)	500 ppm	KCl	1.0 %
Fe(III)	0.5 ppm	KNO_3	0.5 %
HCO_3^-	100 ppm	$NaNO_2$	0.5 %
Mg(II)	100 ppm	Na_2SO_4	1.0 %
Sn(II)	1.0 ppm	NaH_2PO_4	5.0 %
Sn(IV)	0.1 ppm	$HClO_4$	1.0 %
Mn(II)	5.0 ppm	Na_2SO_3	0.01 %

Concentration of each heavy metal was 15 ppb for Cd(II), 50 ppb for Ni(II), 25 ppb for Co(II), 50 ppb for Cu(II), 50 ppb for Bi(III) and 100 ppb for Hg(II).

Table 3 Recovery of the Six Heavy Metal Ions from Composite Sample in the Presence of Sixteen Foreign Ions or Salts

Ion	Taken (ppb)	Found (ppb)	Recovery (%)	C.V. (%)
Cd(II)	15.9	15.7 ± 0.2	99.4	1.2
Ni(II)	50.0	50.4 ± 0.6	100.8	1.2
Co(II)	25.0	25.2 ± 0.1	100.8	0.5
Cu(II)	50.0	50.7 ± 0.4	101.5	0.7
Bi(III)	50.0	49.6 ± 0.4	99.2	0.9
Hg(II)	100.0	100.9 ± 0.9	100.9	0.9

Coexistent ions(ppm) and salts(%)

Ag(I) 0.1, Ca(II) 50, Cr(III) 0.5, Fe(III) 0.05, Mg(II) 50, As(III) 10, Mn(II) 0.5. Sn(II) 0.1, Sr(II) 10, Zn(II) 0.05, HCO_3^- 10, $HClO_4$ 0.01, KCl 0.1, KNO_3 0.01, NaCl 0.1, $NaNO_2$ 0.01

Table 4 Analytical Results of Metal Ions in River Water Samples

Sample	Method	Concentration ($\bar{x}$ ± s, ppb)*		
		Cd(II)	Co(II)	Cu(II)
Tamatani River	HPLC	2.3 ± 0.0	3.6 ± 0.1	460 ± 4
	FL-AAS	2.0 ± 0.2	< 10	453 ± 62
Gôtani River 1	HPLC	0.9 ± 0.0	1.5 ± 0.1	319 ± 4
	FL-AAS	< 1	< 10	320 ± 23
Gôtani River 2	HPLC	0.4 ± 0.0	1.3 ± 0.1	132 ± 1
	FL-AAS	< 1	< 10	127 ± 12
Kakehashi River	HPLC	0.7 ± 0.1	1.4 ± 0.1	40 ± 1
	FL-AAS	< 1	< 10	44 ± 3

* : average value ± standard deviation, N = 4

FL-AAS conditions

Dry : 25 A, 30 sec, Ash : Cd;30 A, 30 sec, Co,Cu;80 A, 30 sec, Atomize : Cd;150 A, 8 sec, Co,Cu;300 A, 10 sec

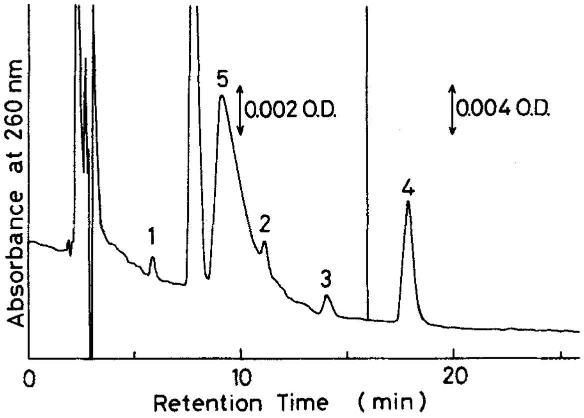


FIGURE 4 Typical Chromatogram Obtained by River Water Samples
1 : Cd(0.7 ppb), 2 : Ni(1.4 ppb), 3 : Co(1.4 ppb),
4 : Cu(40 ppb), 5 : Zn
* : changing of detector range
Other HPLC conditions were same as Fig. 2.

The recovery and the coefficient of variation for the determination of the six metals in the composite sample prepared from the standard solution were investigated by means of the recommended method. The determination of these metals was carried out in the presence of sixteen ions or salts. The results were shown in Table 3. The six metals were recovered more than 99.2 %, and the coefficient of variation was in the range of 0.5 - 1.2 % from six repeated extractions.

Application to the Determination of Trace Amount of Metals in River Water

The proposed method was applied to the determination of trace amount of heavy metals in river water samples. The samples were collected from Tamatani, Gôtani and Kakehashi river (Komatsu,Japan) and they adjusted to pH 1 with hydrochloric acid in situ. After the samples were filtered through membrane filters(Toyo Roshi, TM-2, 0.45 μm), the analysis were carried out for 50 ml aliquots of the filtrate by the recommended HPLC method. The analytical results were shown in Table 4 and Fig. 4. The metals in the same samples were also determined by FL-AAS method. Bismuth(III) and mercury (II) in river water samples were not detected by both methods. Nickel was only detected in the Kakehashi River(1.4 ± 0.1) by the HPLC method, but the other samples contained less than 1.0 ppb (corresponding to the detection and determination limits of nickel). As can be seen from Table 4, analytical results obtained by the AAS and the proposed method were good agreed.

DISCUSSION

The proposed method permited the simultaneous determination of ppb levels of cadmium(II), nickel(II), cobalt(II), copper(II), bismuth(III) and mercury(II) in water without receiving serious interference from foreign ions. This method is suitable for a routine analysis, because the method is rapid, simple, precise and accurate. In addition, this method does not require so expensive apparatus and special skillfulness, and has extensive concentration range of working curves (by a factor of 1000). Several metal ions whose concentration were very different were simultaneously determined by only changing the detector range without dilution of samples.

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