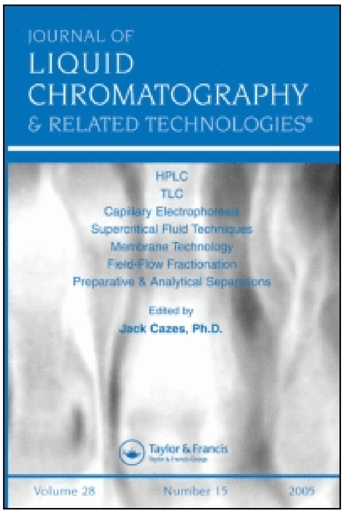

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CONCENTRATION OF HEAVY METALS BY HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

Application of high-speed countercurrent chromatography (HSCCC) to the concentration of metal ions has been studied. The stationary phase, containing di(2-ethylhexyl) phosphoric acid (DEHPA) in n-heptane, was continuously fed into the column. The ppb level of metal ions in a 500 mL of the mobile phase was continuously concentrated into small volumes of the stationary phase retained in the column. Concentrated metal ions were eluted with nitric acid and determined by the emission intensity with a direct current plasma atomic emission spectrometer (DCP-AES). The recoveries of Ca, Cd, Mg, Mn, Pb and Zn ranged over 88% at a concentration of 10 ppb each in 500 mL of the sample solution. Versatility of the present method was further demonstrated in determination of trace metals in tap water and deionized water.

INTRODUCTION

Countercurrent chromatography (CCC) has been widely applied to the separation of many organic materials because of its advantages over other chromatographic methods, such as high sample recovery and no contamination.[1,2] In spite of these advantages, there have been no applications to the separation of inorganic elements until quite recently. However, many of the features of high-speed countercurrent chromatography (HSCCC) have convinced us that this method can be successfully used in separation of inorganic elements and in inorganic analytical chemistry.[3]

We demonstrated the efficient separation, by HSCCC, of adjacent 14 lanthanide elements in an isocratic run using an exponential gradient elution.[4] Also, we achieved the mutual separations of nickel, cobalt, magnesium, and copper; copper, cadmium, and manganese; iron (II) and iron (III); using isocratic elution.[5] Separation of zirconium and hafnium was achieved by Zolotov et al.[6] Separation of ortho- and pyrophosphate ions,[7,9] cesium and strontium,[7] zinc and cadmium[8] were studied by Maryutina et al.

Recently, it has been shown that HSCCC has a great potential in the ultra-trace determination of metals, since it can concentrate minute amounts of metal prior to instrumental multielement analysis, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS).[10,11]

Enrichment of the desired trace elements would not only allow highly sensitive determination of the trace elements, but would also alleviate various problems, including interferences, high risk of exposure to toxic chemicals and radiation from radioactive samples, etc. This paper describes the application of high-speed CCC to the concentration of metal ions.

EXPERIMENTAL

Apparatus

A Shimadzu countercurrent chromatograph (HSCCC-1A, prototype) was used, which holds a monolayer coil separation column on the rotary frame at a distance of 10.0 cm from the central axis of the centrifuge.

The column was prepared from a single piece of approximately 20 m long, 1.60 mm I.D. PTFE (polytetrafluoroethylene) tubing by winding it directly onto the holder hub (10 cm diameter). The beta value, an important parameter used

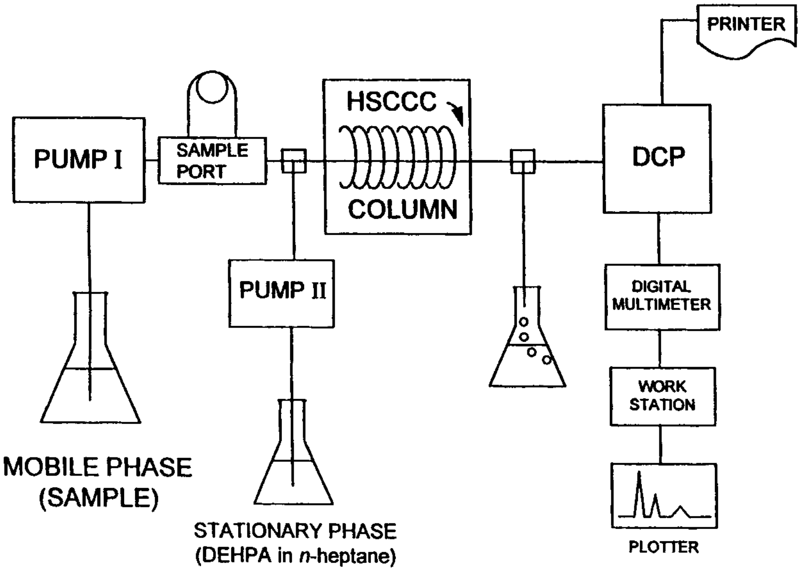

Figure 1. Flow diagram of instrumentation assembly.

to determine the hydrodynamic distribution of the two solvent phases in the rotating coil, was 0.5 in this experiment. It is defined as the ratio of the column radius to the revolution radius. The coil capacity is approximately 40 mL. The HSCCC can be operated at a rotational speed of 800 rpm.

The flow diagram of the experimental assembly is shown in Fig. 1. A Shimadzu LC-6A pump (Pump I) was used to pump the mobile phase. Another Shimadzu LC-6A pump (Pump II) was used to feed the stationary phase into the column. A stream splitter was used for delivering an appropriate amount of effluent to the DCP via a peristaltic pump equipped in the DCP. The DCP-AES system is a SpectraMetrics Model SpectraSpan IIIB system with 20 fixed-wavelength channels for observation of the elution profile.

To facilitate monitoring the elution profile of the single element, an analog recorder signal from the DCP system was converted into a digital signal using a Hewlett Packard Model 3478A digital multimeter. The digital data was stored in a Hewlett Packard Vectra-D Work Station through an HP-IB Bus, and the elution profile was plotted using a Hewlett Packard 7440A graphics plotter and Advanced Graphics Software Slide Write Plus. For simultaneous multi-

Table 1

Wavelengths Used for the Present Work

Element	Line, nm	Element	Line, nm
Ca	315.8	Mn	257.6
Cd	226.5	Ni	341.4
Co	345.3	P	213.6
Cu	324.7	Pb	283.3
Fe	259.9	Zn	206.2
Mg	280.2		

elements measurements, the emission signal for each channel was integrated for 10 seconds at the intervals of 20 seconds, and each set of integrated data was printed out. The data were entered manually to the work station and the elution profile was plotted. Wavelengths used for the present work are listed in Table 1.

Reagents

For the preparation of the two-phase solvent system, analytical reagent grade n-heptane and tartaric acid were purchased from Kanto Chemical Co., Inc., Tokyo Japan and Di- (2-ethylhexyl) phosphoric acid (DEHPA) from Nacalai Tesque, Inc., Kyoto Japan.

Metal standards were obtained as 0.1 M nitric acid or hydrochloric acid solutions (1000 ppm) from Kanto Chemical Co.

Water used in this work was purified by circulating deionized water, prepared by mixed bed resins from tap water, in a Millipore Super-Q System with a train of carbon, mixed bed resins. All other reagents were of analytical-reagent grade.

Preparation of Two Phase Solvent and Sample Solutions

DEHPA was dissolved in n-heptane (stationary phase). Tartaric acid was dissolved in de-ionized water (mobile phase). Sample solutions were prepared by diluting 1000 ppm standard solutions with aqueous tartaric acid.

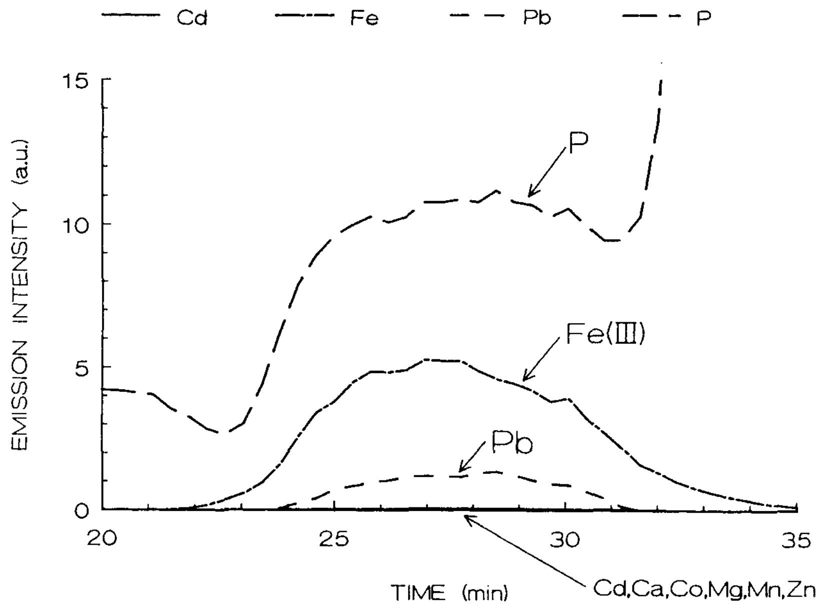

Figure 2. Emission intensities after standard sample injection. The experimental conditions were as follows: apparatus, HSCCC centrifuge with 10.0-cm-revolution radius; column, one monolayer coil, 20 m x 1.60 mm i.d., 40-mL capacity; stationary phase, 0.2 M DEHPA in heptane; mobile phase, 0.1 M tartaric acid; sample, 10 mL of each 10-ppm solution in 0.1 M tartaric acid adjusted pH to 6.2 by ammonia; revolution, 800 rpm; flow rate, 1.3 mL/min.

Procedure

Each concentration was initiated by filling the entire column with the deionized water. After the HSCCC apparatus was started to rotate at 800 rpm in a head-to-tail elution mode, the mobile phase (sample) and the stationary phase were introduced into the column at a flow rate of 5 mL/min and 0.1 mL/min, respectively. Then, concentrated metal ions were eluted with 10 mL of 1 M nitric acid through a sample port, at a flow rate of 1.3 mL/min. Emission signal for each element was obtained by means of on-line monitoring of the effluent using a DCP emission spectrometer. The effluent from the column was divided into two streams with a tee adapter: a peristaltic pump equipped in the DCP emission spectrometer was used to pump the effluent into the DCP at a flow rate of 1.2 mL/min, while the rest of the effluent was discarded. Each concentration was determined by comparing peak area with that of standard.

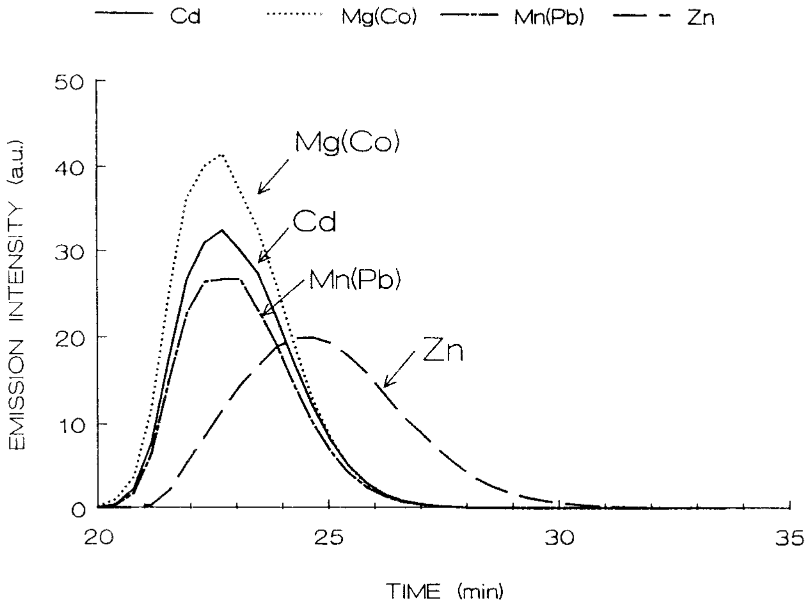

Figure 3. Emission intensities after elution of concentrated metal ions with nitric acid. The experimental conditions were as follows: apparatus, HSCCC centrifuge with 10.0-cm-revolution radius; column, one monolayer coil, 20 m x 1.60 mm i.d., 40-ml capacity; stationary phase, 0.2 M DEHPA in heptane; mobile phase, 10 ml of 0.1 M nitric acid injected by sample port; sample, metals concentrated at column head of HSCCC; revolution, 800 rpm; flow rate, 1.3 ml/min.

RESULTS AND DISCUSSION

Concentration and Elution of the Standard Solutions

In contrast to the separation of metal ions in our previous work,[5] most trace metal ions should be completely extracted into the organic stationary phase for effective concentration of ions. The pH of the sample solution should be adjusted appropriately. As many metal ions are expected to hydrolyze due to weakness of acidity at high pH, tartaric acid was used as complex-forming reagent.

In order to ensure concentration for ppm level standard solution, 10 mL of 10 ppm standard sample in 0.1 M tartaric acid, adjusted pH to 6.2 by ammonia, was injected from the sample port after introducing 10 mL of stationary phase

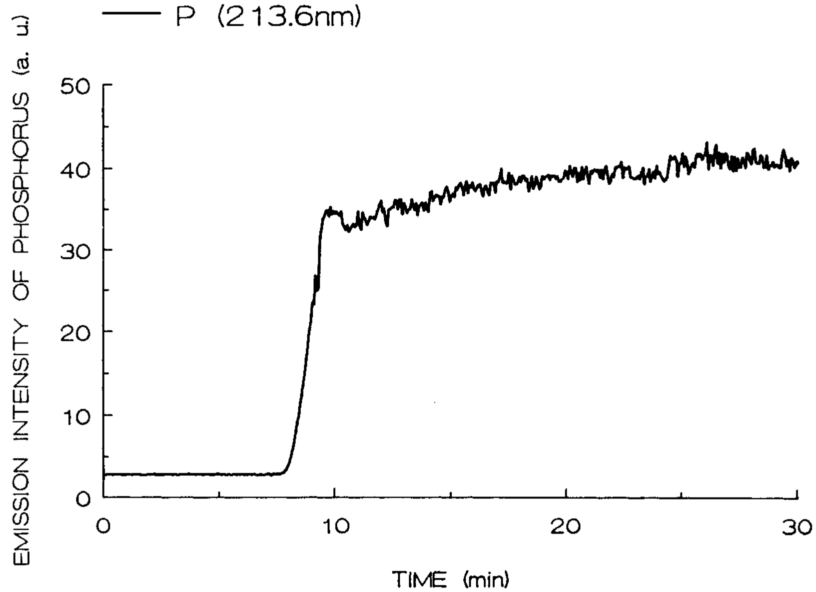

Figure 4. Phosphorus concentration on continuous feeding of stationary phase. The experimental conditions were as follows: apparatus, HSCCC centrifuge with 10.0-cm-revolution radius; column, one monolayer coil, 20 m x 1.60 mm i.d., 40-mL capacity; stationary phase, 0.6 M DEHPA in heptane; mobile phase, 0.1 M ammonium tartrate; revolution, 800 rpm; flow rate of pump I, 5.0 mL/min; flow rate of pump II, 0.1 mL/min.

Table 2

Recovery of Standard Solutions

Sample Conc.	Vol. (mL)	pH	DEHPA Conc.	Recovery of Metal Ions (%)*								
				Ca	Cd	Co	Cu	Mg	Mn	Ni	Pb	Zn
10 ppm	10	6.2	0.2M	86	97	97	97	86	91	44	75	103
10 ppb	500	6.0	0.6M	80	94	61	41	71	75	39	73	102
10 ppb	500	6.7	0.6M	96	109	69	50	88	88	43	93	104
10 ppb	500	8.0	0.6M	73	105	63	44	71	73	47	45	118

*Averages of three experiments.

into the head of the HSCCC column using pump II in Fig. 1, while the mobile phase was pure tartaric acid in this experiment. Figure 2 shows the emission intensity of Ca, Cd, Co, Fe(III), Mg, Mn, P, Pb, and Zn soon after injection. Most of trivalent iron was not extracted. On the other hand, Ca, Cd, Co, Mg, Mn, and Zn were well concentrated in the column.

As shown in Fig. 2, phosphorus concentration is almost constant before the sample injection. However, it is increasing after introducing the sample into the column. This phenomenon shows decreasing the concentration of DEHPA in the stationary phase.

Figure 3 shows the results of elution profiles. Ten mL of 0.1 M nitric acid was injected into the column to elute extracted elements. Most of the extracted elements in Fig. 2 were well eluted with good recovery.

Introduction of Stationary Phase During Operation

To concentrate extremely trace elements, a large quantity of sample must be passed through the column. However, when introducing the mobile phase, the concentration of DEHPA in stationary phase is decreasing as shown in Fig. 2. To prevent the loss of DEHPA, stationary phase was fed continuously. Figure 4 shows the phosphorus concentration when stationary phase was fed at a flow rate of 0.1 mL/min. Eluent flow rate was 5 mL/min.

Using Pump II for continuously introducing the stationary phase, phosphorus concentration, which indicates the concentration of DEHPA in heptane, was almost constant. Also, each metal ion in a large volume of water sample was effectively concentrated in a small amount of organic phase.

Recovery of Standard Samples and Concentration of Real Samples

Figure 5 shows the influence of DEHPA concentration on the recovery of 10 ppb standard. The recovery of each element was calculated from each peak area after elution. Sample was 500 mL of each 10 ppb solution in 0.1M tartaric acid, adjusted to pH 6.0 by ammonia. Stationary phase was 0.6 M DEHPA in heptane, which was continuously introduced into the column. Flow rate was 5 mL/min when sample was concentrated into the column; after concentration of 500 mL (100 min), the flow rate was changed to 1.3 mL/min for the determination of each element, using 10 mL of nitric acid as an eluent.

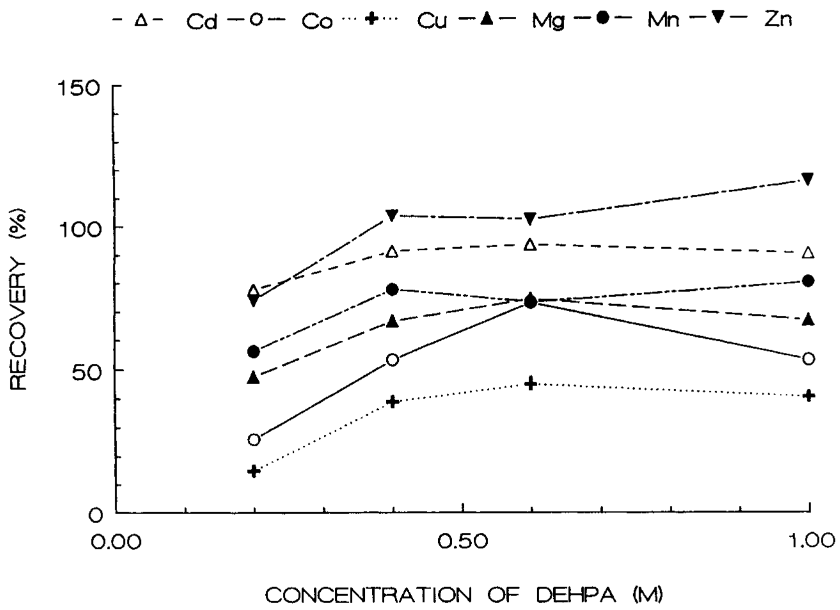

Figure 5. Influence of the DEHPA concentration on the recovery of 10 ppb standard. The experimental conditions were as follows: apparatus, HSCCC centrifuge with 10.0-cm-revolution radius; column, one monolayer coil, 20 m x 1.60 mm i.d., 40-mL capacity; stationary phase, 0.6 M DEHPA in heptane; mobile phase (sample), 500 mL of each 10-ppb solution in 0.1 M tartaric acid adjusted pH to 6.0 by ammonia; revolution, 800 rpm; flow rate of pump I, 5.0 mL/min for concentration of the sample, 1.3 mL/min for the determination using 10 mL of 1 M nitric acid as an eluent; flow rate of pump II, 0.1 mL/min.

Recovery was insufficient at 0.2M DEHPA. However, as the DEHPA concentration was increased, the recovery increased. DEHPA, 0.6 M, was used to concentrate a large volume and trace level sample such as tap or deionized water.

Table 2 shows a summary of recovery for standard solutions at different experimental conditions of sample concentration, DEHPA concentration, and pH. Recovery of 10 mL of 10 ppm sample, injected by sample injector, showed relatively good results, except for Ni and Pb. For concentration of large amounts of sample, pH was a critical factor. At pH 6.7, the recoveries for Ca, Cd, Mg, Mn, Pb, and Zn ranged over 88 %. All recovery values were averages of three experiments.

Table 3

Determination of Trace Metals

Element	Tap Water (ppm)*	Deionized Water (ppm)*
Ca	6.83 (6.12)**	0.0012
Cd	0.0014 (<0.03)**	0.00041
Mg	1.42 (1.47)**	0.00018
Mn	0.0018 (<0.03)**	0.00028
Pb	0.0062 (<0.6)**	0.00052
Zn	0.112 (0.10)**	0.010

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* 500 mL sample was concentrated. ** Found by DCP-AES direct method

Table 3 is an example for determination of a real sample. 500 mL of tap water in our laboratory and deionized water (tap water purified with mixed bed resins) were concentrated by the present method. The results showed the determination values for six elements. Some elements could be determined directly by DCP emission spectrometry. Each value for Ca and Mg shows a good agreement.

HSCCC has great potential as a concentration technique as well as separation technique that preconcentrates trace elements before determination, using instrumental multi-element analysis, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

Enrichment of the desired trace elements prior to determination can not only overcome such problems as interference, toxic, or radioactive samples, etc., but can also provide highly sensitive determination of trace elements.

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