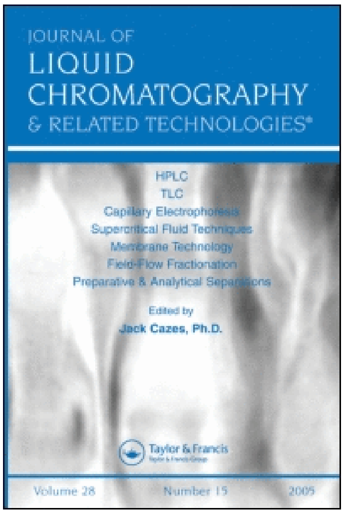

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Separation of Calcium (II), Magnesium (II), Strontium (II), and Barium (II) by High Performance Centrifugal Partition Chromatography with Some Organophosphorus Compounds

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ABSTRACT

Some kinds of organophosphorus compounds were compared for the separation of calcium (II), magnesium (II), strontium (II), and barium (II), in aqueous media by continuous high performance centrifugal partition chromatography (HPCPC). Among extractants investigated, *bis*-2-ethylhexylphosphinic acid (BEHPA) showed the most selective reagent for the extraction and separation of the four alkaline earth metal ions. Well-defined HPCPC separation of the four metal ions, therefore, was performed by

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using a heptane solution of BEHPA as a stationary phase. The mobile phases used were 0.1 M chloroacetic acid solutions (pH 5.30 and 6.50) containing 5% ethanol. The HPCPC system was operated with 2136 partition channels, at a rotational speed of 800 rpm, and at a flow rate of 1.5 cm^3/min.

INTRODUCTION

Organophosphoric acids have often used for the extraction of transition and rare earth metal ions for the purpose of condensation and separation of interesting components from metal mixtures and waste materials.[1–5] Di-2-ethylhexylphosphoric acid (DEHPA) commercially available is one of the widely used reagent to extract a variety of metal ions from aqueous media.[1] More recently, we have introduced di-2-methylnonylphosphoric acid (DMNPA) as an efficient and convenient extractant for the extraction of heavy metal ions.[6] Such dialkylphophinic acids as *bis*-2-ethylhexylphosphinic acid (BEHPA) and *bis*(2, 4, 4-trimethylpenthyl) phophinic acid (BTMPA), on the other hand, have been accepted to be more selective than dialkylphosphoric acids, and therefore, used for the mutual separation of chemically resembled metals in mixture by the conventional liquid–liquid extraction.[4] Here, we first have compared three kinds of alkylphosphorus extractant for the extractability and the degree of separation among calcium (II), magnesium (II), strontium (II), and barium (II) from acidic aqueous solution; these metals have never extensively interested the investigators of separation chemistry.[7,8]

The solvent extraction of the four alkaline earth metal ions has been studied using various extractants, and the mutual separation between Ca(II) and Mg(II) has been reported using DEHPA in kerosene by a counter-current partition extractor.[9] High performance centrifugal partition chromatography (HPCPC) is a multistage liquid–liquid separation technique, applicable to both trace analysis and macro-scale separation.[10–12] Being one of the most useful techniques for the mutual separation of chemically resembling metal ions, HPCPC was attempted to separate the four alkaline earth metal ions in acidic media by using some alkylphosphorus acids/heptane as the stationary phase. The chloroacetic acid mobile phase is used at various pH values. The two-step elution is then applied to perform the separation of the four alkaline earth metal ions. It is demonstrated, that the present HPCPC has some advantages with respect to selectivity, versatility, and convenience.

EXPERIMENTAL

Reagents and Apparatus

Bis-2-ethylhexylphosphinic acid, 2-ethylhexyl 2-ethylhexylphosphonic acid (EHPA), DEHPA, and DMNPA were kindly supplied by Daihachi Chemical Industry Co. Ltd (purity: above 96.6 wt.% for BEHPA, above 95.2 wt.% for EHPA, above 95.0 wt.% for DEHPA, and above 96.0 wt.% for DMNPA). Heptane of reagent grade was used as the organic solvent (Wako Pure Chemical Industry Co. Ltd.). Chloroacetic acid of regent grade was used as the mobile phase (Wako Pure Chemical Ind. Co. Ltd.). 3,3′-Bis[*N*,*N*-*bis*(carboxymethyl)-aminomethyl]-*o*-cresolphthalein (PC, Dojindo Lab.) was employed as the post-label reagent. The other chemicals used were of reagent grade.

A Senshu Science (Tokyo, Japan) HPCPC (Model LLB-M, manufactured by Sanki Eng. Ltd., Kyoto, Japan) was used in this study; it has 2136 partition channels set in a rotor, and the total cell volume was about 230 cm^3. A Shimadzu Model 10AV UV-VIS spectrophotometeric detector was used to monitor the absorbance of the metal chelate formed with PC in the eluate.

Procedure

A heptane solution containing a certain concentration acidic organophosphorus extractant, 50 cm^3, was used as a stationary phase. Under the high performance centrifugal force (usually 800 rpm), a chloroacetic mobile phase was pumped from a rotary seal joint to the stationary phase at a flow-rate of 2.0 $\mathrm{cm}^3/\mathrm{min}$. After equilibration between the two phases, an aliquot of sample solution containing 10^{-4} M, each alkaline metal ion ($\mathrm{pH} > 6.0$) was injected through the sample loop (1.0 cm^3). The eluate was monitored at 575 nm after mixing it with 1.57×10^{-4} M PC as the post-label reagent. The pH of PC solution was adjusted to an appropriate value by adding ammonia and acetic acid.

RESULTS AND DISCUSSION

Principle of High Performance Centrifugal Partition Chromatography Separation

In HPCPC, the retention volume (V_R) is related to the distribution ratio (D) of the desired component between the stationary and mobile phases:

$$V_R = V_m + DV_s \quad (1)$$

where V_s and V_m are the volume of the stationary and mobile phases, respectively. The theoretical plate number (N_M) is also related to the retention volume (V_R) and the bandwidth ($W_{1/2}$):

$$N_M = 5.54\left(\frac{V_R}{W_{1/2}}\right)^2 \tag{2}$$

The separation factor (α_c) is calculated from the retention volumes of individual components 1 and 2:

$$\alpha_c = \frac{V_{R,2} - V_o}{V_{R,1} - V_o} \tag{3}$$

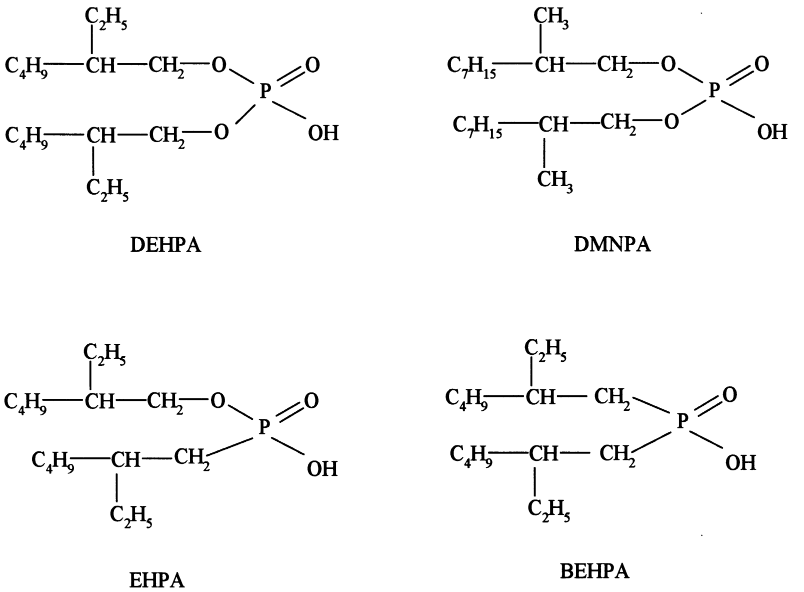
where V_o is the elution volume for an unrestrained component. The degree of separation for two adjacent bands is defined as peak resolution (R_s);

$$R_s = 1.18\left(\frac{V_{R,2} - V_{R,1}}{W_{1/2,1} + W_{1/2,2}}\right) \tag{4}$$

If the fundamental parameters for individual metal ions are known, we can predict the possibility of desired separation between two metal ions of interest. We studied the effect of rotational speed, flow rate of the mobile phase, and volume ratio of the stationary and mobile phases on the HPCPC separation. The standard experimental conditions for HPCPC separation were 2136 partition channels of the rotor, a heptane stationary volume of 50 cm^3, a rotational speed of 800 rpm, and a flow rate of 2.0 cm^3/min.

Comparison of Acidic Organophosphorus Extractants for the Separation of the Four Alkaline Earth Metal Ions by High Performance Centrifugal Partition Chromatography

Acidic organophosphorus extractants have some advantages in HPCPC, as well as in solvent extraction: ease of loading and stripping for metal ions, low solubility in the aqueous phase, and relatively large separation factor. The chemical structures of the organophosphorus extractants are shown in Fig. 1. Table 1 lists some physico-chemical constants of these extractants.[2,13] Obviously, the acidity of extractants decreases as the number of oxygen atoms in the dialkylbraches increases, and affects the extractability



DEHPA

DMNPA

EHPA

BEHPA

Figure 1. Chemical structures of acidic organophosphorus extractants used. DEHPA: di-2-ethylhexylphosphoric acid; DMNPA: di-2-methylnonylphosphoric acid; EHPA: 2-ethylhexyl 2-ethylhexylphosphonic acid; BEHPA: *bis*-2-ethylhexylphosphinic acid.

and selectivity of metal ions. The overall extraction equilibrium can be expressed by:

$$M^{2+} + \frac{2+a}{2}(HA)_{2,o} \rightleftharpoons MA_2 \cdot aHA + 2H^+ \tag{5}$$

Table 1. Some physico-chemical constants of acidic organophosphorus extractants.[2,13]

Extractants	Dissociation constant (pK_a)	Distribution constant ($\log K_d$)	Dimerization constant ($\log K_2$)
DEHPA	2.75	3.04	3.54
DMNPA	2.71	4.01	4.01
EHPA	4.85	2.99	4.42
BEHPA	5.94	4.69	1.75

The HPCPC separation of Mg(II), Ca(II), Sr(II), and Ba(II) by DEHPA, DMNPA, EHPA, and BEHPA was investigated by HPCPC, using DEHPA, DMNPA, EHPA, and BEHPA. Figure 2 shows the relationships between log D and pH obtained by HPCPC. Obviously, the half-extraction pH ($pH_{1/2}$) of each metal ion increased in the order of DMNPA < DEHPA < EHPA < BEHPA, which was in accordance with the order of pK_a value for extractants used.

The α_c and $\Delta pH_{1/2}$ values for the four alkaline earth metal ions are summarized in Table 2. The $\Delta pH_{1/2}$ values between two metal ions are often correlated with the configuration of the metal complexes extracted. Danesi et al. pointed out that the selectivity for Co/Ni, depending on extractants used, was due to the steric hindrance of their substituting groups.[1] The selectivity between two metal ions increased in the order of DMNPA < DEHPA < EHPA < BEHPA. Previously, we have reported that DEHPA has a larger steric hindrance than DMNPA,[6] and EHPA than DEHPA.[1] Therefore, the steric hindrance order of the extractants can be thought to be BEHPA > EHPA > DEHPA > DMNPA. **T2**

It can be seen from Fig. 2, that the extractability of each metal ion depended on extractants used, and that the order of Ca(II), Mg(II), Sr(II), and Ba(II) was almost the same with DMNPA, DEHPA, and EHPA, in which Ca(II) has the lowest $pH_{1/2}$ value. The order of extractability for BEHPA as an extractant, however, was Mg(II) < Ca(II) < Sr(II) < Ba(II). The results suggest that Ca(II) is easier to form extractable metal complexes with the dialkylphosphorus acids except for BEHPA, in which chloroacetic acid acts as a weak complexing agent for the extraction of Ca(II). Figure 3 shows the HPCPC separation curve of Ca(II) and Mg(II) using EHPA; the two metal ions are supposed to be separated by HPCPC with DEHPA or DMNPA, because the R_s values were sufficient to separate the two peaks. As a result, BEHPA is demonstrated to be the most selective extractant for the mutual separation of Mg(II), Ca(II), Sr(II), and Ba(II).

Separation of the Four Alkaline Earth Metal Ions by High Performance Centrifugal Partition Chromatography Using *Bis*-2-Ethylhexylphosphinic Acid

The separation of Mg(II) and Ca(II) by HPCPC was investigated at different flow rates. Line (1) and (2) in Fig. 4 show the HPCPC curves obtained at flow rates of 2.0 cm^3/mL and 1.5 cm^3/mL, respectively. Because of the lower α_c value (3.23), the two metal ions could not be separated under such HPCPC conditions as a flow rate of 2.0 cm^3/mL, pH (the mobile phase) = 5.30, and a rotational speed of 800 rpm. By decreasing the flow

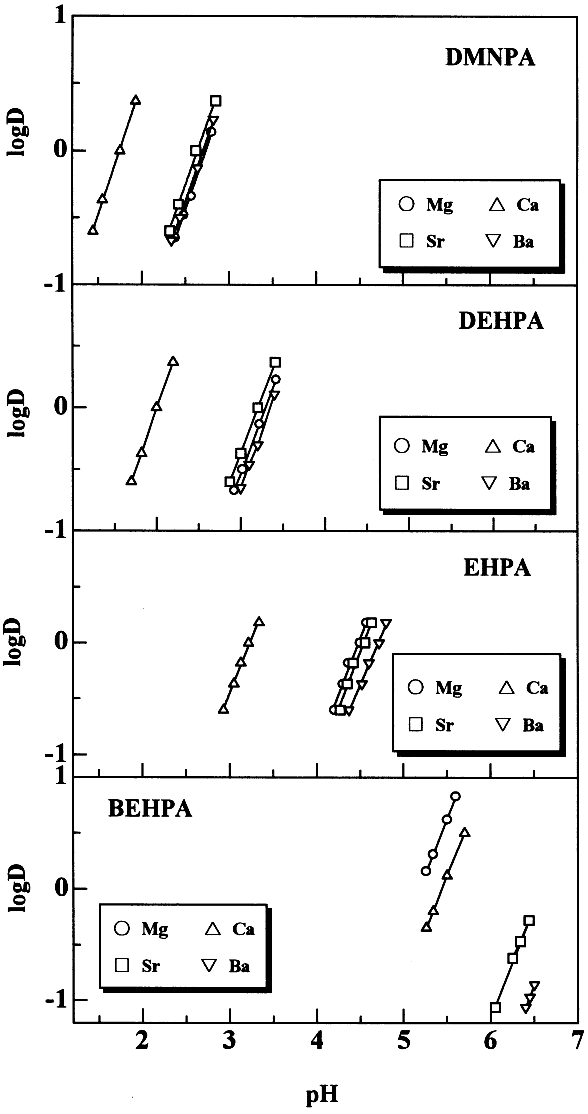


Figure 2. Relationship between log D and pH for alkaline earth metal ions by HPCPC using organophosphorus extractants. Rotational speed: 800 rpm; Flow rate: 2.0 cm^3/min; Partition channel: 2136; Stationary phase: 50 cm^3 of 0.14 M HDEPA; 0.12 M HMNPA; 0.15 M EHPA; 0.16 M BEHPA, respectively. Mobile phase: 0.1 M (H, Na)CH_2ClCOO.

Table 2. Separation factor and $\Delta pH_{1/2}$ of alkaline earth metal ions by HPCPC.

Extractant	M_2–M_1	α_c (D_1/D_2)	$\Delta pH_{1/2}$ ($pH_{1/2,2} - pH_{1/2,1}$)
DMNPA	Mg–Ba	1.11	0.03
	Ba–Sr	1.20	0.06
	Sr–Ca	18.4	0.90
DEHPA	Ba–Mg	1.21	0.06
	Mg–Sr	1.50	0.08
	Sr–Ca	22.6	1.20
EHPA	Ba–Sr	2.01	0.16
	Sr–Mg	1.30	0.05
	Mg–Ca	11.4	1.26
BEHPA	Ba–Sr	5.01	0.33
	Sr–Ca	36.8	1.15
	Ca–Mg	3.23	0.27

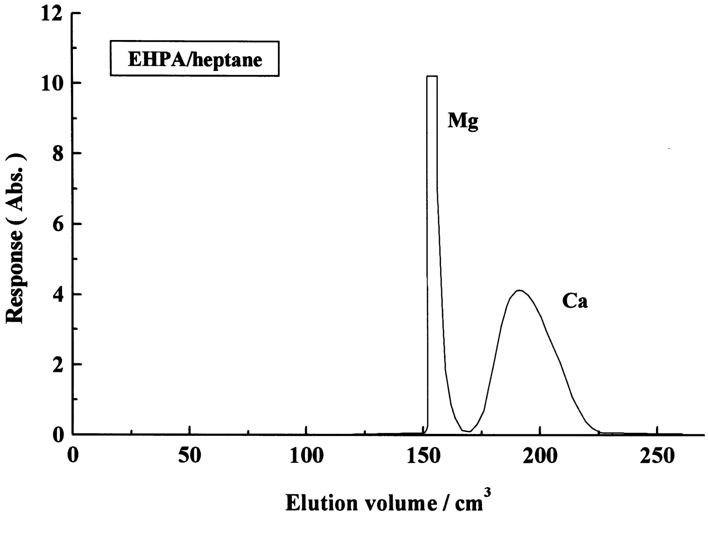


Figure 3. Separation of Mg(II) and Ca(II) by HPCPC using EHPA. Rotational speed: 800 rpm; pH = 3.30; flow rate: 2.0 cm^3/min; Partition channel: 2136; Stationary phase: 50 cm^3 of 0.15 M EHPA; Mobile phase: 0.1 M (H, Na)CH_2ClCOO.

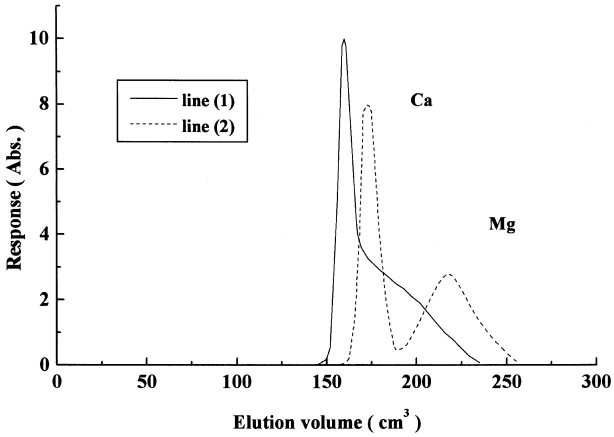


Figure 4. Separation of Mg(II) and Ca(II) by HPCPC using BEHPA. Rotational speed: 800 rpm; Partition channel: 2136; Stationary phase: 50 cm^3 of 0.16 M BEHPA; Mobile phase: 0.1 M (H, Na)CH_2ClCOO. Line (1): pH = 5.30; flow rate: 2.0 cm^3/min; Line (2): pH = 5.30; flow rate: 1.5 cm^3/min.

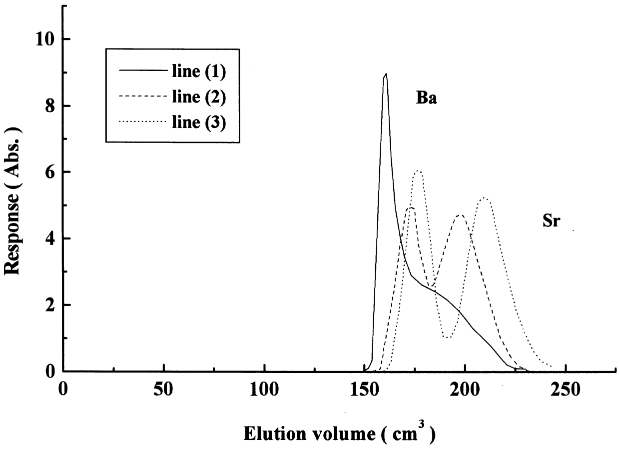


Figure 5. Separation of Sr(II) and Ba(II) by HPCPC using BEHPA employing HPCPC. Rotational speed: 800 rpm; Partition channel: 2136; Stationary phase: 50 cm^3 of 0.16 M BEHPA; Line (1): Mobile phase: 0.1 M (H, Na)CH_2ClCOO, CH_3COO; pH = 6.55; flow rate: 2.0 cm^3/min; Line (2): Mobile phase: 0.1 M (H, Na)CH_2ClCOO, CH_3COO; pH = 6.55; flow rate: 1.5 cm^3/min; Line (3): Mobile phase: 5% EtOH, 0.1 M (H, Na)CH_2ClCOO, CH_3COO; pH = 6.50; flow rate: 1.5 cm^3/min.

rate to 1.5 cm^3/mL, almost complete separation was achieved, in which the theoretical plate number and peak resolution for the two metals were: $N_{Ca} = 1200$, $N_{Mg} = 200$, and $R_s = 1.10$.

Although the α_c value of Sr(II) and Ba(II) was 1.70, the peak separation was incomplete, as shown in Fig. 5, line (1). Even when the flow rate was decreased to 1.5 cm^3/mL, we failed to get complete separation, as shown in Fig. 5, line (2). It would be expected that the reaction of Sr(II) and Ba(II) was relatively slow at higher pH regions, and it needs too much time to reach the extraction equilibrium, which affects the HPCPC separation of the two metal ions. In order to resolve this problem, an amount of 5% ethanol was added to the mobile phase to increase the reaction contact surface area. As expected, almost complete separation was achieved, as shown in Fig. 5, line (3), in which N_M values and R_s were: $N_{Ba} = 880$, $N_{Sr} = 500$, 1.08, respectively. Based on the fundamental results, the HPCPC separation of Mg(II), Ca(II), Sr(II), and Ba(II) in mixture was performed by the two-step elution, as shown in Fig. 6.

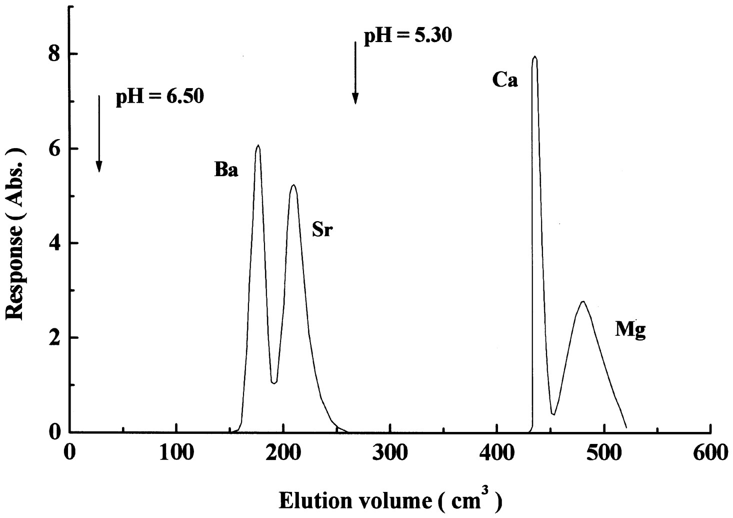


Figure 6. Separation of alkaline earth metal ions by HPCPC using BEHPA. Rotational speed: 800 rpm; Flow rate: 1.5 cm^3/min; Partition channel: 2136; Stationary phase: 50 cm^3 of 0.16 M BEHPA/heptane; Mobile phase: 5% EtOH, 0.1 M (H, Na)CH_2ClCOO, CH_3COO; pH = 6.50; 0.1 M (H, Na)CH_2ClCOO; pH = 5.30.

CONCLUSION

The HPCPC separation of Mg(II), Ca(II), Sr(II), and Ba(II) was investigated by using some acidic organophosphorus extractants. Among them, BEHPA was found to be the most selective, and therefore, was added to the heptane stationary phase for the separation of the four alkaline earth metal ions at room temperature. The chloroacetic acid mobile phases include 5% ethanol, and the pH was adjusted to 6.50 and 5.30. The two-step elution was used to successfully perform the HPCPC separation of the four metal ions. The HPCPC system was operated with 2136 partition channels, at 800 rpm rotational speed, and 1.5 cm^3/min flow rate.

REFERENCES

1. Danesi, P.R.; Yinger, L.R.; Mason, G.; Kaplan, L.; Horwitz, E.P.; Diamond, H. Selectivity-structure trends in the extraction of CO(II) and NI(II) by dialkylphosphoric, dialkylphosphonic, and dialkylphosphinic acids. Solvent Extr. Ion Exch. **1985**, *3*, 435–452.
2. Yao, B.H.; Nagaosa, Y.; Satake, M.; Horita, K.; Nomura, A. Solvent extraction of metal ions and separation of nickel (II) from other metal ions by organophosphorus acids. Solvent Extr. Ion Exch. **1996**, *14*, 849–870.
3. Nagaosa, Y.; Yao, B.H. Extraction equilibria of some transition metal ions by bis(2-ethylhexyl)phosphinic acid. Talanta **1997**, *44*, 327–337.
4. Nagaosa, Y.; Yao, B.H. Solvent extraction of rare-earth metals with bis(2-ethylhexyl)phosphinic acid. Fresenius' J. Anal. Chem. **1997**, *357*, 635–641.
5. Nagaosa, Y.; Yao, B.H. Recovery and separation of lanthanum(III), aluminium(III), cobalt(II) and nickel(II) from misch metal by solvent extraction using bis(2-ethylhexyl)phosphinic acid. Sep. Sci. & Technol. **1997**, *32*, 1053–1065.
6. Wang, T.; Nagaosa, Y. Solvent extraction of some metal ions with di-2-methylnonylphosphoric acid into heptane. J. Chem. Tech. Biotechnol. *in press.*
7. Komatsu, Y.; Umetani, S. Triple-phase separation of alkaline earth metal ions. Anal. Sci. **1997**, *13*, 105–110.
8. Komastu, Y.; Fujiki, Y.; Sasaki, T. Solvent extraction separation of alkaline earth metal ions with thenoyltrifluoroacetone and trioctylphosphine oxide in carbon tetrachloride. Solvent Extr. Ion Exch. **1991**, *9* (3), 471–479.
9. Nagaosa, Y.; Nonome, N. Purification of unrefined nickel(II) sulfate solution by a continuous countercurrent multistage extraction with

bis(2-ethylhexyl)phosphinic acid. J. Chem. Technol. & Biotechnol. **1997**, *69*, 114–120.

10. Hoshi, H.; Nakamura, S.; Akiba, K. Separation of lanthanoids and actinoids by centrifugal partition chromatography. J. Liq. Chromatogr. & Relat. Technol. **1999**, *22*, 1319–1330.
11. Muralidharan, S.; Freiser, H. CPC: tool for practical separation of metals and fundamental investigations of chemical mechanisms. Value Adding Solvent Extr. **1996**, *1*, 427–432.
12. Muralidharan, S.; Freiser, H. Fundamental aspects of metal ions separations by centrifugal partition chromatography. ACS Symp. Ser. **1999**, *716*, 347–389.
13. Wang, T.; Nagaosa, Y. Solvent extraction equilibrium of copper(II) with diisodecylphosphoric acid in heptane and dodecane. Anal. Sci. **2001**, *17*, a401–a404.
14. Qiu, D.Y.; Zheng, L.A.; Ma, R.J. The behaviour-structure relations in the extraction of cobalt(II), nickel(II), copper(II) and calcium(II) by monoacidic organophosphorus extractants. Solvent Extr. Ion Exch. **1989**, *7* (6), 937–950.

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