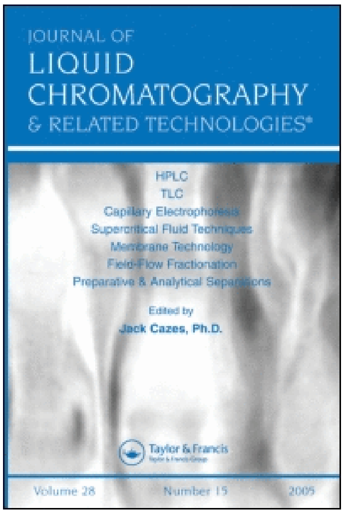

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# Separation of Some Transition Metal Ions by High Performance Centrifugal Partition Chromatography with *bis*-2-Ethylhexylphosphinic Acid

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# Separation of Some Transition Metal Ions by High Performance Centrifugal Partition Chromatography with *bis*-2-Ethylhexylphosphinic Acid

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**Abstract:** The separation of such metal ions as Fe(III), Zn(II), Cu(II), Mn(II), Co(II), and Ni(II) has been investigated by high performance centrifugal partition chromatography (HPCPC) using 0.16 M bis(2-ethylhexyl)phosphinic acid/heptane as a stationary phase. Acetate, chloroacetate, and tartrate buffers were used as mobile phases. The above six metal ions could be well separated by HPCPC using the step elution method, in which the pH of the mobile phases was changed at fixed elution times. The Co(II) cations present in unrefined Ni(II) sulfate solution could also be separated by this HPCPC method. The sample solution was continuously delivered into the stationary phase by a pump, and the Co(II) cations were found to be preferably retained into the stationary phase. The HPCPC system was operated with 2,136 partition channels, at a rotation speed of 800 rpm, and at a flow rate of 2.0 $cm^3$/min.

**Keywords:** Please supply

## INTRODUCTION

Over the past two decades, liquid-liquid extraction and related techniques for metal ions have already been studied using a variety of organophosphorus acids as extractants.[1–3] Previously, we found that bis(2-ethylhexyl)phosphinic acid (BEHPA) had a superior selectivity and extractability for many transition and heavy metal ions.[4–6] We also have studied the purification of unrefined

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Ni(II) solution by countercurrent multistage extraction technique.[7] The separation method, however, included complicate operations and precise control of experimental conditions for the separation of such metal ion impurities as Fe(III), Zn(II), Cu(II), Mn(II), and Co(II), from Ni(II).

Centrifugal partition chromatography is a simple and convenient technique based on the multistage extraction, which enables separation and isolation of metals on laboratory- and industrial-scales.[8–12] High performance centrifugal partition chromatography (HPCPC) is an advanced model using unique circular partition disk packs. The stationary phase (liquid) is retained by centrifugal force in numerous discrete partition channels. The mutual separation among the above six kinds of metal ions in mixture has already been studied by HPCPC using di-2-methylnonylphosphoric acid.[13–15] Furthermore, it is expected that the isolation of metal ion of interest is possible by successive sample injection into the HPCPC system, if the separation factor relative to others is favorably large. Thus, HPCPC can also be used for the purification technique of an unrefined metal ion sample containing impurities as an alternative.

In the present paper, the HPCPC separation of Fe(III), Zn(II), Cu(II), Mn(II), Co(II), and Ni(II) used BEHPA/heptane stationary phase and such mobile phases as acetate or tartrate buffer. The separation of Co(II) from Ni(II) is also investigated by conducting the successive sample injection procedure.

## EXPERIMENTAL

### Reagents

BEHPA was kindly supplied by Daihachi Chemical Industry Co. Ltd (purity: above 96.6%). 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). 4-(2-Pyridylazo)resorcinol (PAR) (Dojindo Lab.) was employed as a post-column derivatization reagent. The other chemicals used were of reagent grade.

### Apparatus

A Senshu Science (Tokyo, Japan) high performance centrifugal partition chromatography (Model LLB-M) was used in this study, which has 2,136 partition channels set vertically in a rotor. One disk pack (16.5 cm long as radius) contains 178 partition channels. One channel is 1.50 cm long, and all channels are connected in series. The total channel volume was 230 $cm^3$. This HPCPC instrument was previously sold under the Sanki trade name and has been abundantly described.[16] A Shimadzu Model 10AV UV-VIS spectrophotometer detector was used to monitor the absorbance of the metal complex at 515 nm; the metal complex eluted from the HPCPC instrument was derivatized with PAR by post-column reaction. A fraction collector (Pharmacia LKB Biotechnology) was also used to collect the purified Ni(II) solution by this HPCPC method.

## Procedures

### Liquid-Liquid Extraction of Transition Metal Ions

Aqueous and organic solutions, 20.0 $cm^3$ each, were taken into a 50-mL separatory funnel, and the two phases were then shaken for 30 min until equilibrium was reached. The initial concentration of metal ion was $5.0 \times 10^{-3}$ M, and the ionic strength of the aqueous phase was kept at 0.10 with 0.10 M chloroacetate. After the two phases were separated completely, the pH value of the aqueous phase was measured. The total concentration of metal ion in the aqueous phase was determined by titration with $5.0 \times 10^{-3}$ M EDTA using Cu-PAN (PAN for $Cu^{2+}$) as an indicator.

### HPCPC Separation of Metal Ion Solution

A heptane solution containing 0.16 M BEHPA, 50 $cm^3$, was used as a stationary phase. Under the centrifugal force (usually 800 rpm), the acetate or tartrate buffer solution as the mobile phase was pumped from a rotary seal joint to the stationary phase at 2.0 $cm^3$/min flow rate in the descending mode. A sample solution containing $5.0 \times 10^{-4}$ M of each metal ion in the mixture was then injected through the sample loop (1.0 $cm^3$). After derivatization with PAR, the eluate was monitored by spectrophotometric detection at 515 nm. The unrefined Ni(II) sulfate sample solution was passed through the stationary phase for the purpose of a continued purification using this HPCPC. The eluted Ni(II) solution was collected by the fraction collector. The Co(II) in the purified Ni(II) sulfate solution was determined by adding suitable amounts of citrate buffer and Nitros-R salt (1-nitroso-2-hydroxy-3,6-naphthalene disodium sulfate), followed by measuring the absorbance of the resultant solution at 420 nm.[17]

## RESULTS AND DISCUSSION

### Separation Factors Among Some Transition Metal Ions

Fe(III), Zn(II), Cu(II), Mn(II), Co(II), and Ni(II) were extracted into 0.16 M BEHPA/heptane from 0.10 M chloroacetate buffer solution, according to the procedure described in the experimental section.[4] Figure 1 shows the

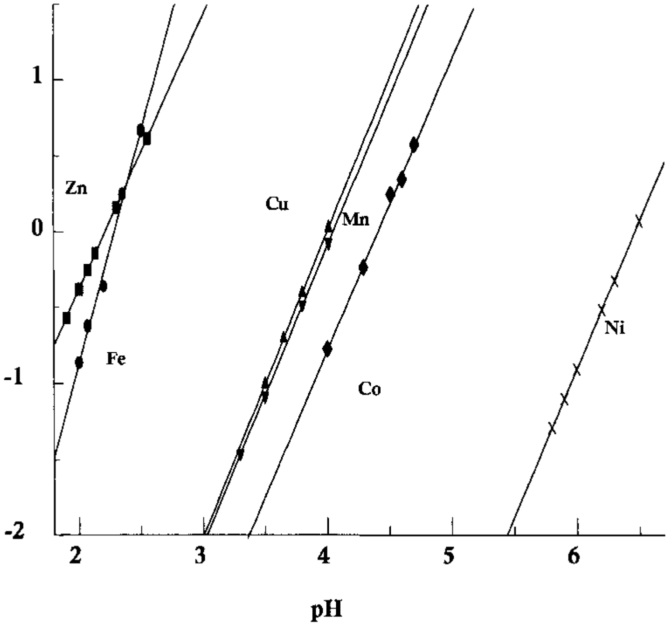

***Figure 1.*** Extraction curves of some metal ions by liquid-liquid extraction. Organic phase: 50 $cm^3$ 0.16 M BEHPA; Aqueous phase: 0.10 M chloroacetate buffer and 0.10 M sulfuric acid.

relationships between log D and pH for six kinds of metal ions investigated, which gave the linear lines with slopes of close to ca. 2.0 and ca. 3.0 for Fe(III). The results are in full agreement with previous works.[17] The half-extraction pH ($pH_{1/2}$) increased in the order of Fe(III) < Zn(II) < Cu(II) < Mn(II) < Co(II) < Ni(II), which coincided with the extractability of the metal ions. We can expect the possibility of HPCPC separation among the metal ions of interest, based on the data on the separation factor ($\alpha_D$) that can be expressed as $D_2/D_1$. The larger the value of $\alpha_D$; generally the easier the extractive separation of the two metal ions. Table 1 summarizes $\alpha_D$ values obtained at the $pH_{1/2}$ values of $M_2$. Data listed in Table 1 suggest that the extractive separation is possible for both Ni(II)-Co(II) and Cu(II)-Zn(II) using BEHPA as the extractant. On the other hand, Mn(II)-Cu(II) and Zn(II)-Fe(III) are expected to be hardly separated by the conventional liquid-liquid extraction method.

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

$$V_R = V_m + D\,V_s \tag{1}$$

*Table 1.* Separation factors for some metal ions by solvent extraction

| Extractant | $M_2 - M_1$ | $\alpha_D$ $(D_1/D_2)$ |
|---|---|---|
| BEHPA | Ni-Co | 10000 |
| | Co-Mn | 4.5 |
| | Mn-Cu | 1.3 |
| | Cu-Zn | 3000 |
| | Zn-Fe | 1.4 (at pH 2.3)<br>10 (at pH 1.5) |

where $V_s$ and $V_m$ are the volumes of the stationary and mobile phases, respectively. In HPCPC, the separation factor ($\alpha_c$) can be also calculated using the retention volumes ($V_{R,1}$ and $V_{R,2}$) of component 1 and 2, respectively:

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

where $V_o$ is the dead volume for a certain chromatographic condition. Since the two separation factors, $\alpha_c$ and $\alpha_D$, are basically identical with each other, we can predict the possibility of separation between two metal ions of interest, if the D values for individual metal ions are known at the working pH.

## Mutual Separation of Some Transition Metal Ions by HPCPC

Since the $\alpha_D$ value for Co(II)-Ni(II) was above $10^4$, HPCPC separation of the two metal ions ($5.0 \times 10^{-4}$ M each, 1.0 $cm^3$ injected volume) was carried out at three different pH values. The other conditions for HPCPC separation were: a heptane stationary phase-volume of 50 $cm^3$, a rotational speed of 800 rpm, and a flow rate of 2.0 $cm^3/min$. As shown in Figure 2, the two metal ions were separated completely with the acetic acid mobile phase at pH values higher than 4.3. Ni(II) peaks remained at almost the same retention volume. Its D value was lower than 0.01 even when the pH of the mobile phase increased from 4.0 to 4.9. Then, it eluted with the dead volume. For the cobalt cation, the D values were 0.12, 0.8, and 7 at the 4, 4.3, and 4.9 mobile phase, explaining the significant changes observed in Figure 2 retention volumes. Mutual separation is complete for mobile phase pHs higher than 4.3.

The separation of Cu(II)-Co(II)-Ni(II) or Mn(II)-Co(II)-Ni(II) was also studied at pH 4.3 by the present HPCPC method. Figure 3 shows the HPCPC chromatograms with the acetate buffer mobile phase (pH 4.3). It

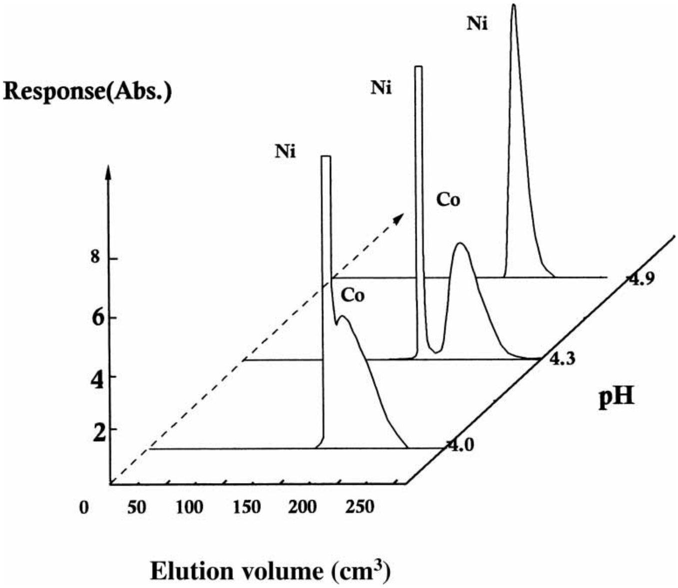

*Figure 2.* Separation of Ni(II) from Co(II) by HPCPC. Sample solution: $5 \times 10^{-4}$ M each metal ion; Stationary phase: 50 $cm^3$ 0.16 M BEHPA; Mobile phase: 0.10 M acetate buffer; Partition channel: 2,136; Rotation speed: 800 rpm; Flow rate: 2.0 $cm^3/min$.

can be seen that the three metal ion mixtures were well separated but Cu(II) and Mn(II) were not, as expected from the separation factors listed in Table 1. Furthermore, it was confirmed that Fe(III) and Zu(II) did not elute at pH 4.3, since their D values were higher than 1000 (Figure 1).

Tartrate buffer as a mobile phase was investigated to separate Cu(II) and Mn(II) by HPCPC, being a complexing agent for some transition metal ions. Figure 4 (B) shows the linear relationships between log D and pH for Cu(II), Mn(II), and Co(II), when 0.02 M tartrate buffer was used as the mobile phase. The Cu(II) line shifted to a higher pH value as the tartrate concentration decreased, overlapping almost with the Co(II), which slightly shifted to the same direction. The degrees of pH shifts for both metal ions were different from each other, depending on the tartrate concentration. On the other hand, the Mn(II) line remained unchanged with 0.02 M tartrate buffer mobile phase in place of the acetate buffer, as shown in Figure 4 (A). There is a much larger difference between Fe(III) and Zn(II) in complex formation with tartrate ion as a ligand. In fact, Fe(III) had no retention with 0.02 M tartrate buffer (pH 6.0) as the mobile phase, and therefore, the separation of Fe(III) from Zn(II) was possible by this HPCPC technique; Zn(II) had no effect on the retention of HPCPC. Based on the experimental results, the HPCPC separation of Fe(III), Zn(II), Cu(II), Mn(II), Co(II), and Ni(II) was

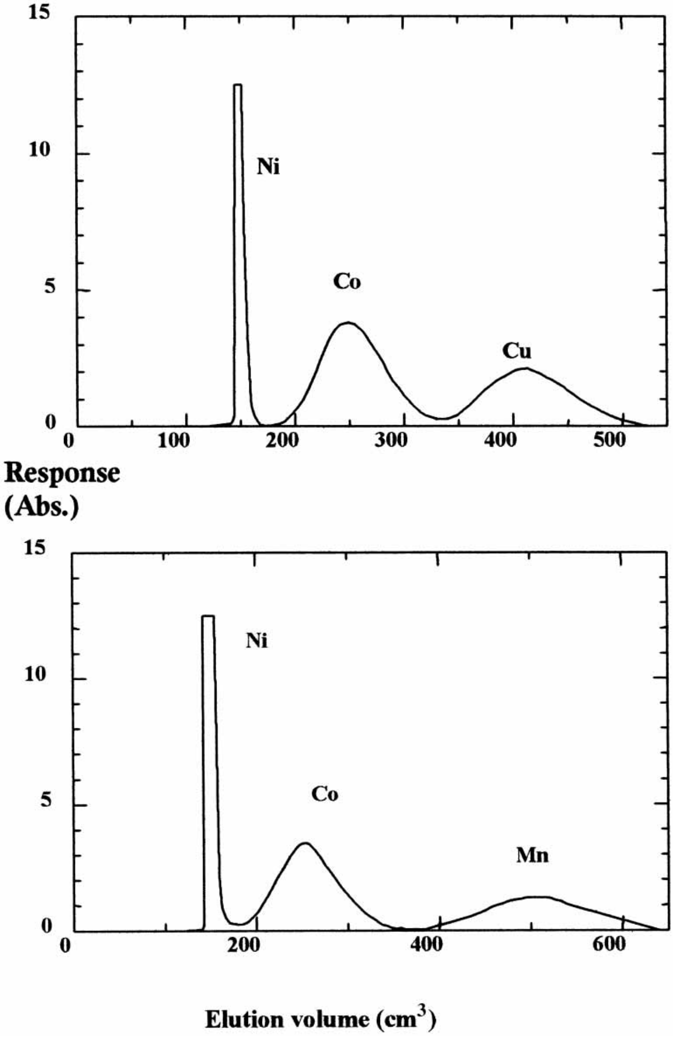

*Figure 3.* Separation of Ni(II), Co(II) and Cu(II) or Mn(II) by HPCPC. Mobile phase: 0.10 M acetate buffer (pH 4.30). The other conditions were the same as those in Figure 2.

studied by using three kinds of 0.10 M tartrate buffer mobile phases (pH 6.25, 4.0, and 1.90). Figure 5 shows the HPCPC chromatogram obtained by the three-pH step elution. The six metal ions were found to be well separated, although Cu(II) and Co(II) coeluted with 0.02 M tartrate buffer mobile phase (pH 4.0); the HPCPC separation for the two metal ions was possible with acetate buffer, as shown in Figure 3.

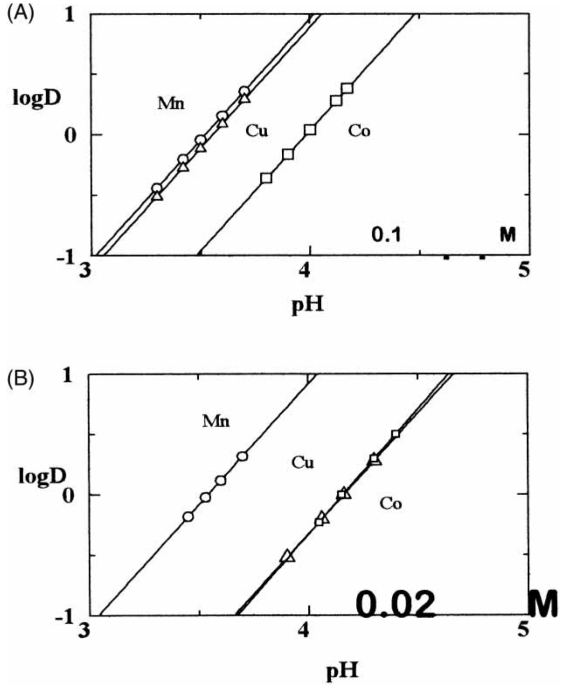

*Figure 4.* Relationship between log D and pH for Mn(II), Cu(II) and Co(II) obtained by HPCPC. (A): 0.10 M acetate buffer mobile phase; (B): 0.02 M tartrate buffer. The other conditions were the same as those in Figure 2.

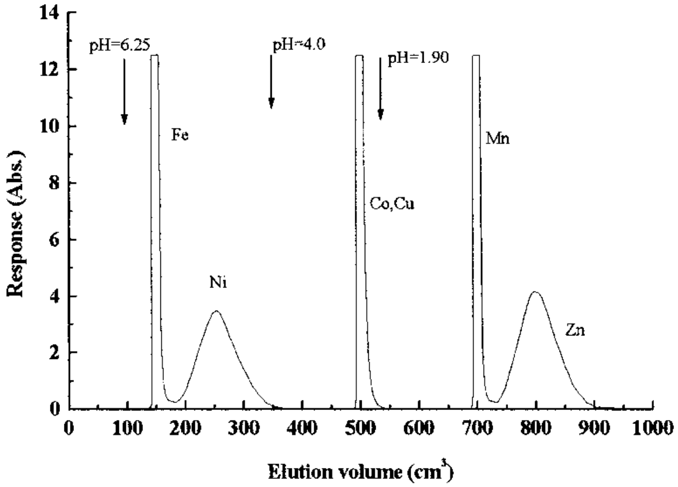

*Figure 5.* Separation of Fe(III), Ni(II), Co(II), Cu(II), Mn(II), Zn(II) by HPCPC. 0.10 M tartrate were used as the mobile phases (pH 6.25, 4.00, and 1.90). The other conditions were the same as those in Figure 2.

## Separation of Cobalt(II) from Nickel(II) Sulfate Solution by HPCPC

The separation of Co(II) from the unrefined Ni(II) solution has been investigated using the displacement procedure described in Ref. 17. Co(II), $1.0 \times 10^{-3}$ M, as a sample solution was continuously pumped into the HPCPC system under the experimental conditions: 800 rotational speed, $2.0\,\mathrm{cm}^3/\mathrm{min}$ flow rate, and pH 4.9. The elution curve is shown as Figure 6, line (1). The retention volume of deionized eluent was about 1,640 $\mathrm{cm}^3$ at which volume the stationary phase was saturated with Co(II). Co(II), 1.64 mM, ions reacted with the 8 mM BEHPA in the heptane stationary phase. The percentage of the reacted BEHPA with the metal ion was calculated to be only 20%. A sample solution containing $1.0 \times 10^{-2}$ M Ni(II) and $1.0 \times 10^{-3}$ M Co(II) (pH 5.5) was successively passed through the stationary phase under the same conditions as that in line (1). It can be seen from Figure 6, line (2), that the Co(II) retention volume for the unrefined Ni(II) sulfate solution decreased by about half, as compared with that for only $1.0 \times 10^{-3}$ M Co(II). This is probably because an excess of Ni(II) reacts with BEHPA to interfere with the retention of Co(II). A sample volume of 900 $\mathrm{cm}^3$ could be treated for purification of the unrefined Ni(II) sulfate solution by using this HPCPC procedure.

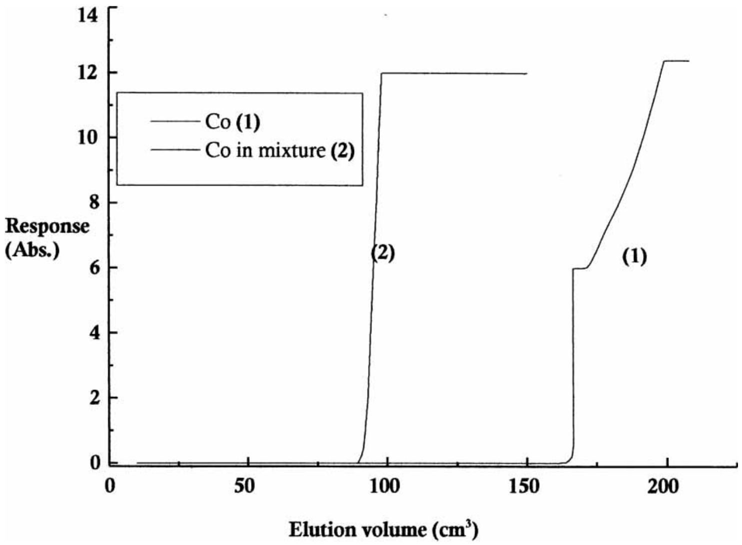

*Figure 6.* Purification of unrefined Ni(II) sulfate solution by HPCPC. Line (1): $1 \times 10^{-3}$ M Co(II) only; pH = 5.90; Line(2): $1 \times 10^{-2}$ M Ni(II) and $1 \times 10^{-3}$ M Co(II); pH = 5.50; The other conditions were the same as those in Figure 2.

## CONCLUSIONS

Fifty $cm^3$ of 0.16 M BEHPA solution in heptane were used as the stationary phase for the separation of metal ions in mixture and Co(II) from the unrefined Ni(II) sulfate by the present HPCPC method. The six kinds of metal ions could mutually be separated, except Cu(II)-Co(II), by the three pH-step-elution method. About 900 $cm^3$ of $1.0 \times 10^{-2}$ M of the unrefined Ni(II) sulfate solution were purified by successive removal of the coexisting Co(II). Being a simple and convenient way of separation, the HPCPC method would enable separation of aqueous sample solution containing those metal ions on preparative or mini-plant scales.

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