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Extraction and Separation of Precious Metals by a Column Packed with Divinylbenzene Homopolymeric Microcapsule Containing Tri-*n*-octylamine

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Extraction and Separation of Precious Metals by a Column Packed with Divinylbenzene Homopolymeric Microcapsule Containing Tri-*n*-octylamine

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ABSTRACT

The separation of palladium, platinum, and gold was investigated using a column packed with divinylbenzene homopolymeric microcapsules containing tri-*n*-octylamine (TOA). The extraction of precious metals except platinum using the microcapsules progresses by means of the same reaction

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proposed in a solvent extraction system. The microcapsules also effectively extracted precious metals from an aqueous hydrochloric acid medium in the column operation. The breakthrough point is delayed in the following order: platinum, palladium, and gold. Almost all TOA molecules enclosed in the microcapsules can act on the extraction reaction with precious metals, which was confirmed by the calculation of the concentration of precious metals extracted into the microcapsules based on the breakthrough curve of each precious metal. By selecting the appropriate eluent, palladium, gold, and platinum were successfully eluted from the column using an 8.0 mol/dm^3 aqueous HCl solution, a 0.1 mol/dm^3 thiourea in 0.1 mol/dm^3 aqueous HCl solution, and a 0.5 mol/dm^3 ethylenediamine in 0.1 mol/dm^3 aqueous NaOH solution, respectively. By feeding the eluent stepwise into the column in this order, the mutual separation of precious metals can be successfully achieved.

Key Words: Microcapsules; Extraction; Column operation; Precious metals; Tri-*n*-octylamine.

INTRODUCTION

Microencapsulation is a unique technique for enclosing active reagents in a porous polymeric membrane,^[1–3] and it has been extensively studied in regard to the elongation of the sustained release of core materials,^[1,4–9] the protection of the encapsulating active-reagents,^[10] and the extraction of metal ions and acids.^[1,8,11–20] Microcapsules encapsulating extractants are expected to be effective separation media for various substances such as metals, inorganic and organic acids, amino acids, and other substances that have been applied to solvent extraction systems, because of the high separation property of the encapsulated extractant, which has been clarified in the solvent extraction system, and because of the high capacity of the extracted chemicals utilizing their internal core. We have previously reported the preparation of microcapsules containing extractants and their extraction properties.^[12–14,18,19] The extraction property of propionic acid using poly(styrene-co-divinylbenzene) copolymeric microcapsules enclosing tri-*n*-octylamine (TOA), which is an extractant for mineral and organic acids and various metal complex anions,^[21] is found to be same as that of the solvent extraction system.^[12] Recently, we successfully prepared divinylbenzene (DVB) homopolymeric microcapsules (poly-DVB microcapsules) with highly porous membranes enclosing TOA by in-situ polymerization accompanied by an evaporation process using volatile solvents.^[18,19] The macropores in the wall of the poly-DVB microcapsules function effectively as channels for extraction, with the microcapsules successfully extracting hydrochloric acid



and precious metals. Furthermore, the extraction equilibrium of palladium(II) using the microcapsules is explained by the same mechanism proposed by the solvent extraction system.^[19] In this paper, poly-DVB microcapsules containing TOA are applied for column operation in order to extract and separate precious metals. The breakthrough properties of palladium(II), gold(III), and platinum(IV) from a column packed with the microcapsules, the elution of the precious metals from the column using eluent reagents, and the mutual separation of the precious metals by selective elution from the column are investigated.

EXPERIMENTAL

Materials

DVB used as a monomer was purchased from Wako Pure Chemicals Industries Co. (Osaka, Japan) and purified by distillation under a reduced-pressure nitrogen atmosphere. The distilled DVB was stored in a refrigerator until it was used. 2,2'-Azobis(2,4-dimethylvaleronitrile) (ADVN) as a radical initiator and TOA as an extractant were obtained from Wako Pure Chemical Industries Co. and were used without further purification. Toluene and gum arabic were used without further purification. Reagent grades of hydrochloric acid, thiourea, ethylenediamine, 25% ammonia aqueous solution, palladium(II) chloride, hydrogen hexachloroplatinate(IV) hexahydrate, and sodium tetrachloroaurate(III) dihydrate were also purchased from Wako Pure Chemical Industries Co. and used as received.

Poly-DVB microcapsules containing TOA were prepared by in-situ polymerization accompanied by toluene evaporation using the same procedure and same conditions as described in our previous paper.^[19] The holdup of the dispersed organic phase, ϕ , was 0.12. The continuous phase was 2.0 wt% aqueous gum arabic solution. The preparation conditions and behaviors of the poly-DVB microcapsules are listed in Table 1.

Extraction Equilibrium of Precious Metals

All experiments regarding extraction equilibrium were carried out batchwise. The microcapsules were pretreated with 0.2 mol/dm³ aqueous HCl solution in order to change all TOA molecules to an ammonium chloride salt. The pretreated microcapsules were immersed in the aqueous HCl solution containing precious metals. The amount of the microcapsules added to the aqueous solution was 40 g/dm³. The concentration of precious metals in the aqueous



Table 1. Preparation conditions of poly(DVB) microcapsules containing TOA.

	MC-2	MC-3	MC-4	MC-5
Dispersed organic phase				
C_{DVB} [mol/dm ³]	1.60	1.06	2.10	3.15
Core solution				
	TOA- Toluene	TOA- Toluene	TOA- Toluene	TOA- Toluene
C_B (mol/dm ³)	1.14	1.14	1.14	1.14
$\phi(-)$	0.12	0.12	0.12	0.12
$C_{B,MC}$ (mol/kg-MC)	1.71	2.02	1.44	1.01
Continuous aqueous phase				
Gum arabic content (wt%)	2.0	2.0	2.0	2.0
Average diameter, d_p (μ m)	159	161	197	192

solution was determined by means of an atomic adsorption spectrometer (AA-625, Shimadzu Ltd., Kyoto, Japan). The concentration of the metals extracted into the microcapsules was estimated based on the mass balance of the metals in the aqueous solution before and after the extraction.

Column Operation of Extraction and Elution of Precious Metals

The microcapsules, which were pretreated with HCl, were packed into a glass column surrounded by a water jacket and having a 10 mm inner diameter. The column was maintained at 303 K. For the breakthrough experiments, 0.2 mol/dm³ aqueous HCl solution containing precious metals at 5.0 mmol/dm³ was fed into the top of the column by a microtubing pump at a constant flow rate. The eluents were collected at given intervals, and the metal concentration was determined by means of an atomic adsorption spectrometer. The loading ratio for extraction was defined as a molar ratio of the quantity of precious metal extracted to 1/ n of the initial TOA quantity in the microcapsules. The value of n is the number of TOA molecules that react with the precious metal chloride complex ion, $n = 2$ for palladium(II) and platinum(IV), $n = 1$ for gold(III).

For the elution experiments, prior to use in the column operation, the microcapsules were immersed in 0.2 mol/dm³ aqueous HCl solution containing precious metals and attained extraction equilibrium. One gram of the microcapsules for extracting the precious metals was packed into the column. The eluents used in this study were 8.0 mol/dm³ aqueous HCl solution,

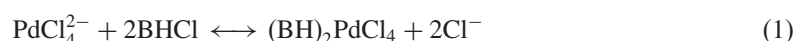


0.01 mol/dm³ aqueous NaOH solution, 0.5 mol/dm³ ethylenediamine diluted in 0.1 mol/dm³ aqueous NaOH solution, and 0.1 mol/dm³ thiourea diluted in 0.1 mol/dm³ aqueous HCl solution. The effluent samples were collected at appropriate intervals, and the concentration of precious metals was determined by an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

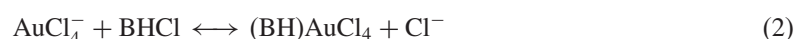
Extraction Equilibrium of Precious Metals Using the Poly-DVB Microcapsules

The extraction of palladium(II) using the poly-DVB microcapsules containing TOA is expressed as follows:^[19]

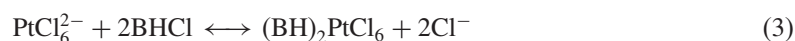


where BHCl is an ammonium chloride salt of TOA.

Gold(III) and platinum(IV) from the hydrochloric acid solution were measured at various concentrations of hydrochloric acid and a fixed initial metal concentration of 5 mmol/dm³. The effect of hydrochloric acid concentration on the distribution ratio of gold (III) and platinum (IV), which is the molar ratio of precious metals between those contained in the microcapsules and in the aqueous phase, $D_M = C_{M,MC}/C_{M,aq}$, is shown in Fig. 1 together with the result of palladium(II). The distribution ratio of gold(III) decreased almost linearly with the increase in the concentration of hydrochloric acid, the slope being about -1 . This result shows that the extraction equilibrium of gold(III) by the microcapsules would be expressed by the same extraction reaction as that proposed in the solvent extraction system^[22] as follows:



On the other hand, the distribution ratio for platinum(IV) slightly decreased with an increase in the concentration of hydrochloric acid. The effect of the HCl concentration on the distribution ratio was, however, considerably less than that estimated based on the result of the solvent extraction system, which would be estimated as having a linear relationship with a slope of -2 . This result indicates that other reactions in addition to the following reaction of platinum(IV) with TOA proposed in consideration of the result of the solvent extraction system^[23] may have occurred:



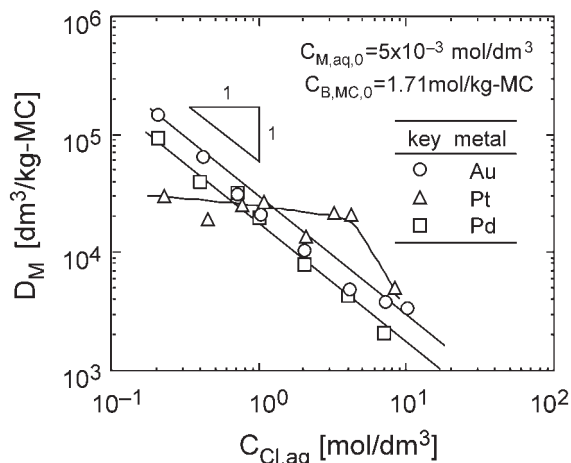


Figure 1. Effect of the chloride ion concentration on the distribution ratios of gold(III) and platinum(IV).

The details of the extraction mechanism of platinum(IV) by TOA enclosed into the microcapsules remain unclear. Further investigation is needed regarding the unusual extraction equilibrium of palladium(IV) by the microcapsules containing TOA.

Breakthrough Profiles of Precious Metals

Breakthrough studies of single precious metals using a column packed with the poly-DVB microcapsules containing TOA were then carried out. Figure 2 shows the typical breakthrough curves for palladium(II), gold(III), and platinum(IV) obtained at a 0.2 mol/dm³ aqueous HCl solution containing 5.0 mmol/dm³ precious metal. The breakthrough point of platinum(IV) appeared at an elution weight of 100 g after the operation started; for palladium(II) the elution weight was 250 g, and for gold(III) it was 500 g. The order in the delay of the breakthrough point for each precious metal agreed with the order of the equilibrium constant of the reaction between precious metal and ammonium salt of TOA as shown by Eqs. 1–3 obtained in the solvent extraction system.^[22–24]

The effect of flow rate on the breakthrough curve of palladium(II) is shown in Fig. 3. With an increase in the flow rate, the breakthrough point of palladium(II) appeared earlier. This suggests the rate-determining step of



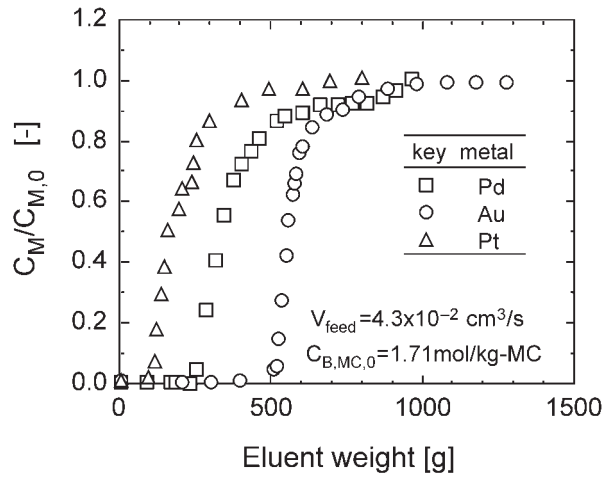


Figure 2. Breakthrough curves of palladium(III), gold(III), and platinum(IV).

palladium(II) extraction can be a liquid film diffusion controlled step.^[20] However, the delay of the saturation point, where the concentration of palladium(II) is same as that at the inlet of the column, was not clearly observed. The effect of the TOA concentration in the microcapsules on the breakthrough curve of palladium(II) is shown in Fig. 4. The breakthrough

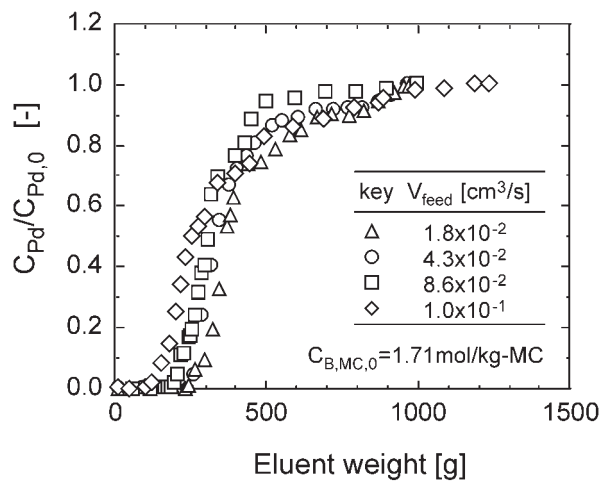


Figure 3. Effect of flow rate on breakthrough curve of palladium(II).

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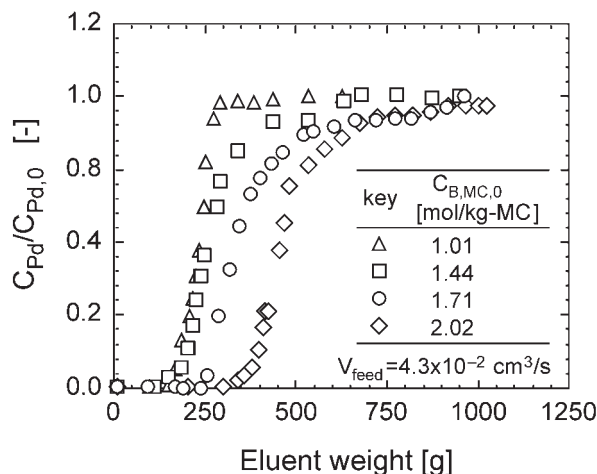


Figure 4. Effect of TOA concentration on breakthrough curve of palladium(II).

point of palladium(II) was delayed with an increase in the TOA concentration. The difference of the results at between 1.01 and 1.44 mol/kg-MC was smaller than those at between 1.44 and 1.71 mol/kg-MC. This difference may be raised from the difference in the size of the microcapsules, which would affect the intraparticle diffusion steps in the extraction of precious metals. Further investigation is necessary for the analysis of the kinetic mechanism on the extraction with the microcapsules prepared.

The total amount of precious metals extracted in the microcapsules was determined by numerical integration using a spline function method. The results of the breakthrough experiment are shown in Table 2. It is clear that the values of the loading ratio are quite high in all experimental conditions. This shows that almost all TOA molecules enclosed in the microcapsules are used in the extraction reaction of precious metals and that the inactivation of the extractant, which has been reported on extractant-impregnated resin,^[25] has not occurred.

Elution of Precious Metal from Column

The possibility of separating palladium, gold, and platinum in the elution step was investigated. It has been confirmed that the extraction of palladium(II) by the microcapsules containing TOA occurred reversibly by the reaction expressed by Eq. (1).^[19] The elution of palladium from



Table 2. Results of breakthrough experiments of precious metals.

Metal	$C_{B,MC,0}$ (mol/ kg-MC)	Weight of MC (g)	Bed height (cm)	Flow rate, V_{feed} (cm^3/s)	$C_{M,MC}$ (mol/ kg-MC)	Loading ratio (-)
Pd	1.01	2.0	4.9	4.3×10^{-2}	0.58	1.1
	1.44	2.0	4.9	4.3×10^{-2}	0.72	1.0
	1.71	2.0	4.9	4.3×10^{-2}	0.99	1.2
	2.02	2.0	4.9	4.3×10^{-2}	1.25	1.2
	1.71	2.0	4.9	1.8×10^{-2}	1.09	1.3
	1.71	2.0	4.9	8.6×10^{-2}	0.99	0.98
	1.71	2.0	4.9	1.0×10^{-1}	0.87	1.0
	1.71	1.0	2.5	4.3×10^{-2}	1.08	1.3
	1.71	3.0	7.8	4.3×10^{-2}	0.98	1.1
Au	1.71	2.0	4.9	4.3×10^{-2}	1.3	0.78
Pt	1.71	2.0	4.9	4.3×10^{-2}	0.52	0.61

the microcapsules was carried out using various concentrations of HCl solution (Fig. 5). When the HCl concentration was 1.0 mol/dm^3 , the elution of palladium could not take place completely. As the HCl concentration was increased, the concentration of palladium in the eluent solution increased and the time necessary for the elution of palladium was shortened. When 8.0 mol/dm^3 of HCl solution was used, palladium was detected from the

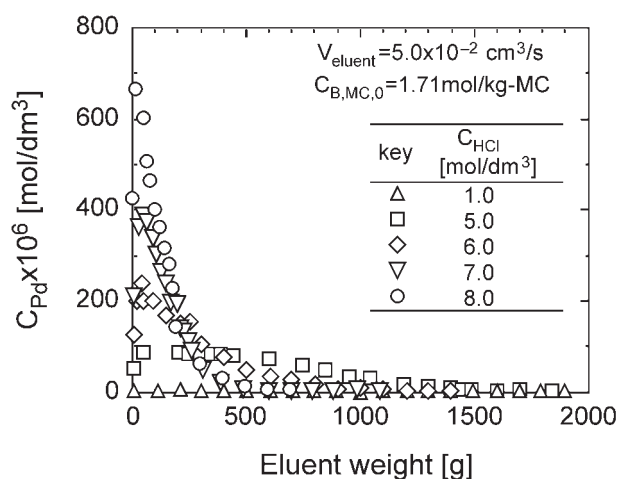


Figure 5. Effect of HCl concentration on elution of palladium.



first fraction of the eluent. This means that the reaction of palladium stripping by 8.0 mol/dm^3 HCl solution, shown by the back reaction of Eq. (1), is relatively fast. As a result, the palladium was recovered completely from the microcapsules within a short period. The amount of palladium recovered as determined by numerical integration of the elution curve was almost equal to the amount of palladium extracted initially into the microcapsules. Figure 6 shows the results of the elution of gold and platinum by 8.0 mol/dm^3 HCl solution together with that of palladium. Gold was not completely eluted by the HCl solution. A slight elution of platinum was observed; however, its concentration in the eluent was very low over a long period. The results achieved by the solvent extraction system show that the extraction reaction of platinum(IV) with TOA occurred reversibly.^[23] This result indicates that the stripping reaction rate of platinum by HCl is very slow. Thus, it is clear that the use of 8.0 mol/dm^{-3} HCl solution can elute palladium only.

The following two methods were considered for the selection of eluents for platinum and gold. One is the use of aqueous alkaline solution as an eluent and the other is the use of a water-soluble chelating reagent such as thiourea and ethylenediamine, which are known to form stable complexes with precious metal chloride ions.^[26,27] The elution of gold using a 0.1 mol/dm^3 aqueous HCl solution containing 0.1 mol/dm^3 thiourea was carried out as shown in Fig. 7. The elution of gold could be achieved within a short period. Thiourea has an ability to reduce gold(III) to gold(I) with the

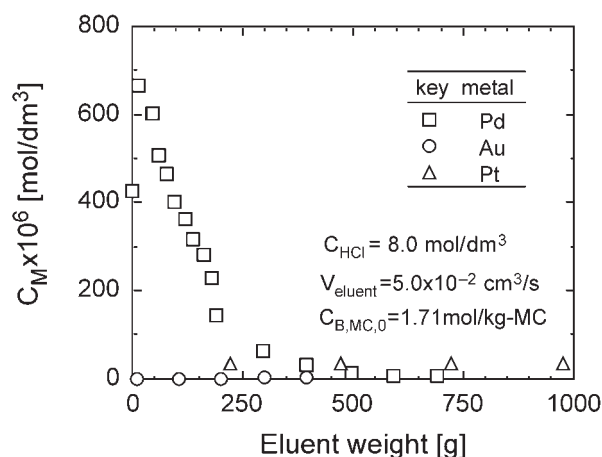


Figure 6. Elution curves of palladium, gold, and platinum using 8.0 mol/dm^3 HCl aqueous solution.



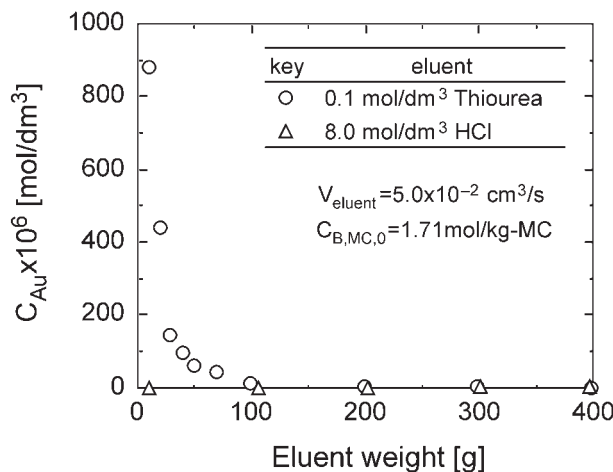


Figure 7. Elution curves of gold using 0.1 mol/dm³ thiourea dissolving in 0.1 mol/dm³ HCl aqueous solution and 8.0 mol/dm³ HCl aqueous solution.

formation of formamidine as the oxidation product and forms strong cationic complexes with gold(I).^[26] The same reaction could occur in this elution of gold from the column using a 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea.

The elution of platinum using some eluents was carried out as shown in Fig. 8. When a 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine was used, platinum was eluted from the column. The elution curve of platinum was, however, broadened compared with the elution curves of palladium and gold. This suggests that the stripping reaction rate between platinum and ethylenediamine is relatively slow. When a 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea or a 0.01 mol/dm³ aqueous NaOH solution was used for the elution, though platinum was eluted, its concentration was very low over a long period. This suggests that the stripping rate of platinum by both of these eluents is very slow. The numerical integration of the elution curves of gold and platinum by thiourea–HCl and ethylenediamine–NaOH solutions shows that all of the gold and platinum extracted into the microcapsule was completely eluted.

From the results regarding the selection of eluents, it was found that an 8.0 mol/dm³ HCl solution is suitable for the elution of palladium, a 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea is suitable for gold, and a 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine is suitable for platinum.



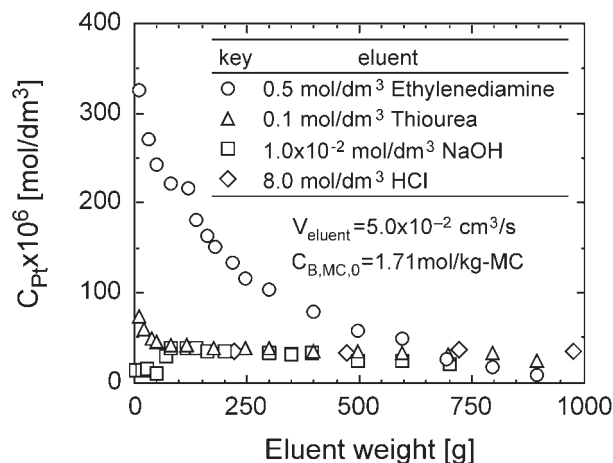


Figure 8. Elution curves of platinum using 0.5 mol/dm³ ethylenediamine dissolving in 0.1 mol/dm³ NaOH aqueous solution, 0.1 mol/dm³ thiourea dissolving in 0.1 mol/dm³ HCl aqueous solution, 1.0 × 10⁻² mol/dm³ NaOH aqueous solution, and 8.0 mol/dm³ HCl aqueous solution.

Mutual Separation and Recovery of Precious Metals by Selective Elution

The results concerning the elution in a single metal system allow us to propose the separation and recovery process of palladium, platinum, and gold in the elution stage, taking advantage of the differences in stripping equilibrium and stripping rate. The separations by elution were carried out in binary systems of palladium/gold and palladium/platinum. The elution curves of palladium and gold in the binary system are shown in Fig. 9. Palladium and gold were completely separated by passing 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea through the column after passing about 500 g of 8.0 mol/dm³ aqueous HCl solution. The highest concentration of palladium in the eluent by 8.0 mol/dm³ aqueous HCl solution was $2.5 \times 10^{-4} \text{ mol/dm}^3$ with no contamination of gold. In the meantime, the highest concentration of gold in the eluent by 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea was $1.4 \times 10^{-3} \text{ mol/dm}^3$ with no contamination of palladium.

The results of the palladium/platinum binary system are shown in Fig. 10. The separation of palladium and platinum was satisfactorily carried out by passing a 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine through the column after passing about 600 g of 8.0 mol/dm³



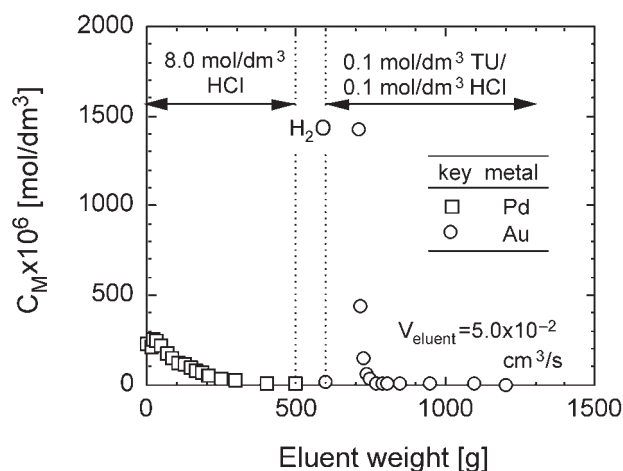


Figure 9. Elution curves of palladium and gold in binary system using 8.0 mol/dm³ HCl aqueous solution and 0.1 mol/dm³ thiourea (TU) dissolving in 0.1 mol/dm³ HCl aqueous solution.

aqueous HCl solution. Leakage of platinum was, however, seen in the stage of palladium elution using an 8.0 mol/dm³ aqueous HCl solution. The highest concentration of palladium in the eluent by 8.0 mol/dm³ aqueous HCl solution was 4.2×10^{-4} mol/dm³ and its purity was 95%. The decrease in purity is due to the elution of platinum. The highest concentration of platinum in the eluent by 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine was 2.6×10^{-4} mol/dm³ with no contamination of palladium.

Finally, the separation of precious metals in palladium/gold/platinum ternary system was carried out. At first, an 8.0 mol/dm³ aqueous HCl solution was fed to the column in order to elute palladium. Next, a 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea for the elution of gold was passed through the column, followed by a 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine for platinum. The elution curves of palladium, gold, and platinum are shown in Fig. 11. Palladium, gold, and platinum were successfully separated by selective elution from the column by coupling the desired elution solution with each precious metal. The highest concentration of palladium in the eluent by 8.0 mol/dm³ aqueous HCl solution was 3.6×10^{-4} mol/dm³ and its purity was 92%. The decrease in purity is due to the elution of platinum. The highest concentration of gold in the eluent by 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea was 1.3×10^{-3} mol/dm³ and its purity was 93%, which contained 7% of palladium. The elution of 8.0 mol/dm³ aqueous HCl



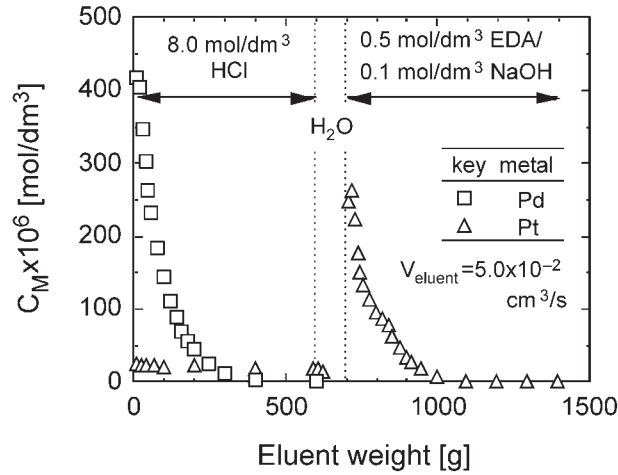


Figure 10. Elution curves of palladium and platinum in binary system using 8.0 mol/dm^3 HCl aqueous solution and 0.5 mol/dm^3 ethylenediamine (EDA) dissolving in 0.1 mol/dm^3 NaOH aqueous solution.

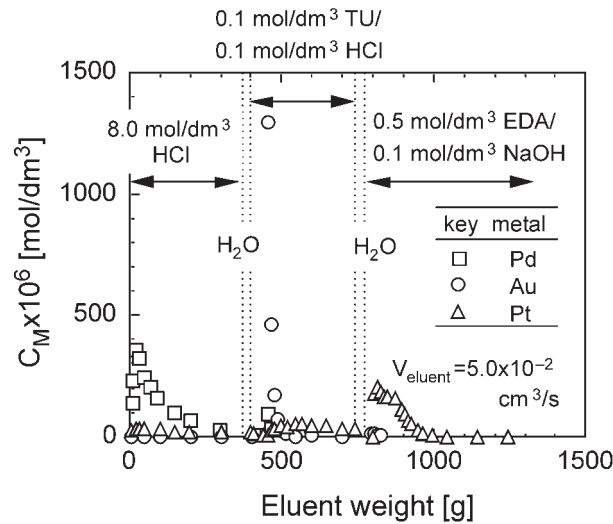


Figure 11. Elution curves of palladium, gold, and platinum in ternary system using 8.0 mol/dm^3 HCl aqueous solution, 0.1 mol/dm^3 thiourea (TU) dissolving in 0.1 mol/dm^3 HCl aqueous solution, and 0.5 mol/dm^3 ethylenediamine (EDA) dissolving in 0.1 mol/dm^3 NaOH aqueous solution.

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solution in this experiment might be unsatisfactory for the complete elution of palladium. The highest concentration of platinum in the eluent by 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine was 2.0 × 10⁻⁴ mol/dm³ and its purity was 97%, which contained 3% of gold.

CONCLUSION

The poly-DVB microcapsules containing TOA were used for in a column operation for extracting palladium(II), gold(III), and platinum(IV). The microcapsules successfully extracted each precious metal without the inactivation of the extractant. By using an 8.0 mol/dm³ aqueous HCl solution for palladium, a 0.1 mol/dm³ aqueous HCl solution containing 0.1 mol/dm³ thiourea for gold, and a 0.1 mol/dm³ aqueous NaOH solution containing 0.5 mol/dm³ ethylenediamine for platinum as eluent solutions, the extracted precious metals can be successfully eluted from the column. The mutual separation of precious metals by selective elution, which is carried out by means of a stepwise feed of the suitable eluent for each precious metal in the above order, was successfully achieved.

NOMENCLATURE

<i>C</i>	Concentration (mol/dm ³ or mol/kg-MC)
<i>d</i>	Average diameter (μm)
<i>D</i>	Distribution ratio (dm ³ /kg-MC)
<i>V</i>	Flow rate (cm ³ /sec)
<i>ϕ</i>	Holdup of the dispersed organic phase (—)

Subscript

0	Initial
aq	Aqueous phase
B	TOA
Cl	Chloride ion
	eluent
	Eluent
feed	Feed solution
DVB	Divinylbenzene
HCl	Hydrochloric acid



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M Precious metal
 MC Microcapsule
 p Particle

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