



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

メタデータ	言語: eng 出版者: Taylor & Francis 公開日: 2007-10-21 キーワード (Ja): キーワード (En): 作成者: Shiomori, Koichiro, Fujikubo, Kenji, Kawano, Yoshinobu, Hatate, Yasuo, Kitamura, Yoshiro, Yoshizawa, Hidekazu メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/10458/782">http://hdl.handle.net/10458/782</a>

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

**Hidekazu Yoshizawa<sup>1)</sup>, Koichiro Shiomori<sup>2\*)</sup>, Kenji Fujikubo<sup>3)</sup>,  
Yoshinobu Kawano<sup>2)</sup>, Yasuo Hatate<sup>3)</sup>, and Yoshiro Kitamura<sup>1)</sup>**

- 1) Department of Environmental Chemistry & Materials, Faculty of Environmental Science & Technology, Okayama University, 3-1-1 Tsushima-Naka, Okayama 700-8530, Japan
- 2) Department of Applied Chemistry, Faculty of Engineering, Miyazaki University, 1-1 Gakuenkihanadai-Nishi, Miyazaki 889-2192, Japan
- 3) Department of Applied Chemistry & Chemical Engineering, Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890-0065, Japan

\*Corresponding author: **Koichiro SHIOMORI**

**e-mail: shiomori@cc.miyazaki-u.ac.jp**

**Temporarily address until 15 Sep. 2003:** Department of Biotechnology, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, S-221 00 Lund Sweden

Tel: +46-46-2220882, Fax: +46-46 224713

**After 15 Sep. 2003:** Department of Applied Chemistry, Department of Applied Chemistry, Faculty of Engineering, Miyazaki University, 1-1 Gakuenkihanadai-Nishi, Miyazaki 889-2192, Japan

Tel: +81-985-58-7309, Fax: +81-985-58-7323

## **ABSTRACT**

The separation of palladium, platinum, and gold was investigated using a column packed with divinylbenzene homopolymeric microcapsules containing tri-n-octylamine. The extraction of precious metals except platinum using the microcapsules progresses by means of the same reaction 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 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  $8.0 \text{ mol}\cdot\text{dm}^{-3}$  aqueous HCl solution, a  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  thiourea in  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  aqueous HCl solution, and a  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  ethylenediamine in  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  aqueous NaOH solution, respectively. By feeding the eluent step-wise into the column in this order, the mutual separation of precious metals can be successfully achieved.

## **Keywords**

Microcapsules, Extraction, Column operation, Precious metals, Tri-n-octylamine

## INTRODUCTION

Microencapsulation is a unique technique for enclosing active reagents in a porous polymeric membrane (11, 22, 24), and has been extensively studied in regard to the elongation of the sustained release of core materials (1, 4, 8-11, 23), the protection of the encapsulating active-reagents (2), and the extraction of metal ions and acids (5-7, 10-15, 19, 20, 27). 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 which 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 (6, 7, 12, 19, 20). 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 (3), is found to be same as that of solvent extraction system (6). Recently, we successfully prepared divinylbenzene homopolymeric microcapsules (poly-DVB microcapsules) with highly porous membranes enclosing TOA by *in-situ* polymerization accompanied by an evaporation process using volatile solvents (19, 20). 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 (20). 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**

Divinylbenzene (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 tri-*n*-octylamine (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 previous paper (20). The holdup of the dispersed phase 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 metal**

All experiments regarding extraction equilibrium were carried out batchwise. The microcapsules were pretreated with  $0.2 \text{ mol/dm}^3$  aqueous HCl solution in order to change all TOA molecules to an ammoniumchloride 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  $40 \text{ g/dm}^3$ . The concentration of

precious metals in the aqueous 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/dm<sup>3</sup> aqueous HCl solution containing precious metals at 5.0 mmol/dm<sup>3</sup> 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 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 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/dm<sup>3</sup> aqueous HCl solution containing precious metals and attained extraction equilibrium. One g of the microcapsules for extracting the precious metals was packed into the column. The eluents used in this study were 8.0 mol/dm<sup>3</sup> aqueous HCl solution, 0.01 mol/dm<sup>3</sup> aqueous NaOH solution, 0.5 mol/dm<sup>3</sup> ethylenediamine diluted in 0.1 mol/dm<sup>3</sup> aqueous NaOH solution, and 0.1 mol/dm<sup>3</sup> thiourea diluted in 0.1 mol/dm<sup>3</sup> 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 (20):



where BHCl is an ammoniumchloride 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/dm<sup>3</sup>. 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 **Figure 1**. 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 (25) 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 (18) may have occurred:



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  $0.2 \text{ mol/dm}^3$  aqueous HCl solution containing  $5.0 \text{ mmol/dm}^3$  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 250g, and for gold (III) 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, 2, and 3 obtained in the solvent extraction system (17, 18, 25).

The effect of flow rate on the breakthrough curve of palladium (II) is shown in **Figure 3**. With an increase in the flow rate, the breakthrough point of palladium (II) appeared earlier, and the saturation point, where the concentration of palladium (II) is same as that at the inlet of the column, was delayed. This suggests the rate-determining step of palladium (II) extraction might be a liquid film diffusion controlled step (27). The effect of the TOA concentration in the microcapsules on the breakthrough curve of palladium (II) is shown in **Figure 4**. The breakthrough point of palladium (II) was delayed with an increase in the TOA concentration. 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 (16), 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 (20). The elution of palladium from the microcapsules was carried out using various concentrations of HCl solution (**Figure 5**). When the HCl concentration was 1.0 mol/dm<sup>3</sup>, 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<sup>3</sup> of HCl solution was used, palladium was detected from the first fraction of the eluent. This means that the reaction of palladium stripping by 8.0 mol/dm<sup>3</sup> 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<sup>3</sup> 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 (18). This result indicate that the stripping reaction rate of platinum by HCl is very slow. Thus, it is clear that the use of 8.0 mol·dm<sup>-3</sup> 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 (21, 26). The elution of gold using a 0.1 mol/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea was carried out as shown in **Figure 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 formation of formamidine as the oxidation product and forms strong cationic complexes with gold (I) (21). The same reaction could occur in this elution of gold from the column using a 0.1 mol/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea.

The elution of platinum using some eluents was carried out as shown in **Figure 8**. When a 0.1 mol/dm<sup>3</sup> aqueous NaOH solution containing 0.5 mol/dm<sup>3</sup> 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/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea or a 0.01 mol/dm<sup>3</sup> 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 were completely eluted.

From the results regarding the selection of eluents, it was found that an 8.0 mol/dm<sup>3</sup> HCl solution is suitable for the elution of palladium, a 0.1 mol/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea is suitable for gold, and a 0.1 mol/dm<sup>3</sup> aqueous NaOH solution containing 0.5 mol/dm<sup>3</sup> ethylenediamine is suitable for platinum.

### **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 **Figure 9**. Palladium and gold were completely separated by passing 0.1 mol/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea through the column after passing about 500 g of 8.0 mol/dm<sup>3</sup> aqueous HCl solution.

The results of palladium/platinum binary system are shown in **Figure 10**. The separation of palladium and platinum was satisfactorily carried out by passing a 0.1 mol/dm<sup>3</sup> aqueous NaOH solution containing 0.5 mol/dm<sup>3</sup> ethylenediamine through the column after passing about 600 g of 8.0 mol/dm<sup>3</sup> aqueous HCl solution. Leakage of platinum was, however, seen in the stage of palladium elution using an 8.0 mol/dm<sup>3</sup> aqueous HCl solution.

Finally, the separation of precious metals in palladium/gold/platinum ternary system was carried out. At first, an 8.0 mol/dm<sup>3</sup> aqueous HCl solution was fed to the column in order to elute palladium. Next, a 0.1 mol/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea for the elution of gold was passed through the column, followed by a 0.1 mol/dm<sup>3</sup> aqueous NaOH solution containing 0.5 mol/dm<sup>3</sup> ethylenediamine for platinum. The elution curves of palladium, gold, and platinum are shown in **Figure 11**. Palladium, gold and platinum were successfully separated by selective elution from the column by coupling the desired elution solution with each precious metal.

## 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/dm<sup>3</sup> aqueous HCl solution for palladium, a 0.1 mol/dm<sup>3</sup> aqueous HCl solution containing 0.1 mol/dm<sup>3</sup> thiourea for gold, and a 0.1 mol/dm<sup>3</sup> aqueous NaOH solution containing 0.5 mol/dm<sup>3</sup> 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 step-wise feed of the suitable eluent for each precious metal in the above order, was successfully achieved.

## REFERENCES

- 1) Sakakura C.; Takahashi, T.; Hagihara, A.; Itoh, M.; Sasabe, T.; Lee, M.; Shobayashi, S. Controlled and Release of Cisplatin from lactic Acid Oligomer Microspheres Incorporating Cisplatin: *In Vitro* Study. *J Control. Release* **1992**, 22, 69-74.
- 2) O'shea, G. M.; Goosen, M. F. A.; Sun, A. M. Prolonged Survival of Transplanted Islets of Langerhans Encapsulated in A Biocompatible Membrane. *Biochim. Biophys. Acta* 1984, **804**, 133-136
- 3) Tanaka, M.; Akaiwa, H. *Youbai Chushutsu Kagaku*; Shokabo Co.: Tokyo, 2000; 109-117.
- 4) Zhou, M. X.; Chang, T. M. S. Control Release of Prostaglandin E2 from Polylactic Acid Microcapsules, Microparticles and Modified Microparticles. *J. Microencapsulation* **1988**, 5, 27-36.
- 5) Watarai, H.; Hatakeyama, S. Extraction of Copper(II) into Microcapsules Containing 5-Nonyl Salicylaldehyde. *Analy. Sci.* **1991**, 7 (3), 487-488.
- 6) Yoshizawa, H.; Uemura, Y.; Kawano, Y.; Hatate, Y. Preparation and Extraction Properties of Microcapsules Containing Tri-n-octylamine as Core Material. *J. Chem. Eng. Japan* **1993**, 26 (2), 198-204.

- 7) Yoshizawa, H.; Uemura, Y.; Kawano, Y.; Hatate, Y. Regeneration of Styrene-Divinylbenzene Copolymer Microcapsule Containing Tri-*n*-octylamine. *J. Chem. Eng. Japan* **1993**, 26 (6), 692-697.
- 8) Cohen, S.; Yoshioka, T.; Lucarelli, M.; Hwang, L. H.; Langer, R. Controlled Delivery System for Proteins Based on Poly(Lactic/Glycolic Acid) Microcapsules. *Pharm. Res.* **1991**, 8, 713-720.
- 9) Hatate, Y.; Kasamatsu, K.; Uemura, Y.; Ijichi, K.; Kawano, Y.; Yoshizawa, H. Controlled Release of Copolymer Microcapsules by Phase Transformation of Encapsulated Stearic Acid. *J. Chem. Eng., Japan* **1994**, 27 (4), 479-484.
- 10) Nishihama, S.; Sakaguchi, N.; Hirai, T.; Komasaawa, I. Extraction and Separation of Rare Earth Metals Using Microcapsules Containing Bis (2-Ethylhexyl) Phosphinic Acid. *Hydrometallurgy* **2002**, 64 (1), 35-42.
- 11) Kondo, T. Microcapsules: Their Science and Technology Part III. Industrial, Medical, and Pharmaceutical Applications. *J. Oleo Sci.* **2001**, 50 (3), 143-152.
- 12) Yoshizawa, H.; Uemura, Y.; Kawano, Y.; Hatate, Y. Stripping Rate of Propionic Acid from Styrene-Divinylbenzene Copolymeric Microcapsules with Tri-*n*-octyl Amine as Core Material. *Solv. Extr. Ion Exch.* **1995**, 13 (2), 333-351.
- 13) Matsumoto, M.; Kondo, K. Application of Microcapsules Containing Extractants to the Extractive Fermentation. *Solv. Extr. Res. Devel. Japan* **2001**, 8, 113-119.
- 14) Kamio, E.; Matsumoto, M.; Kondo, K. Extraction Mechanism of Rare Metals with Microcapsules Containing Organophosphorus Compounds. *J. Chem. Eng., Japan* **2002**, 35(2), 178-185.
- 15) Laguecir, A.; Ernst, B.; Frere, Y.; Danicher, L.; Burgard, M. Extraction of Metal Cations by Polyterephthalamide Microcapsules Containing a Poly(acrylic acid) Gel. *J. Microencapsulation* **2002**, 19 (1), 17-28.

- 16) Akita, S.; Takeuchi, H. Sorption and Separation of Metals from Aqueous Solution by A Macromolecular Resin Containing Tri-n-octylamine. *J. Chem. Eng., Japan* **1990**, 23 (4), 439-443.
- 17) Kawano, Y.; Osada, S.; Shiomori, K.; Baba, Y.; Kondo, K.; Yoshizawa, H.; Hatate, Y. Distribution Equilibrium of Palladium Between Aqueous Hydrochloric Acid Solution and Tri-n-octylamine in Toluene. *J. Chem. Eng., Japan* **1995**, 28(2), 227-230.
- 18) Yoshizawa, H.; Shiomori, K.; Yamada, S.; Baba, Y.; Kawano, Y.; Kondo, K.; Hatate, Y. Solvent Extraction of Platinum(IV) from Aqueous Acidic Chloride Medium with Tri-n-octylamine in Toluene. *Solv. Extra. Res. Develop., Japan* **1997**, 4, 157-166.
- 19) Yoshizawa, H.; Fujukubo, K.; Uemura, Y.; Kawano, Y.; Kondo, K.; Hatate, Y. Preparation of Divinyl Benzene Homopolymeric Microcapsules by In Situ Polymerization with Solvent Evaporation. *J. Chem. Eng., Japan* **1995**, 28 (1), 78-84.
- 20) Shiomori, K.; Yoshizawa, H.; Fujikubo, K.; Kawano, Y.; Hatate, Y.; Kitamura, Y.; Extraction Equilibrium of Precious Metals from Aqueous Acidic Solutions Using Divinylbenzene Homopolymeric Microcapsules Encapsulating Ternary Amine as a Core Material. *Sep Sci. Technol.* in press.
- 21) Argiropoulos, G.; Catrall, R.W.; Hamilton, I. C.; Kolev, S. D.; Paimin R., The Study of a Membrane for Extracting Gold(III) from Hydrochloric Acid Solutions, *J. Membr. Sci.*, **1998**, 138, 279-285.
- 22) Kiyoyama, S.; Shiomori, K.; Kawano, Y.; Hatate, Y. Preparation of Microcapsules and Control of Their Morphology. *J. Microencapsulation* **2003**, 20(4), 497-508.
- 23) Kiyoyama, S.; Ueno, H.; Shiomori, K.; Kawano, Y.; Hatate, Y. Preparation of Cross-Linked Microcapsules Entrapping Inorganic Salt by in-situ Polymerization in (W/O/W) Emulsion System. *J. Chem. Eng., Japan* **2001**, 34(1), 36-42.

- 24) Shiomori, K.; Kawano, Y.; Kiyoyama, S.; Yoshizawa, H.; Uemura, Y.; Hatate, Y. Effective Entrapment of Protein into Polylactide Microcapsule by Solvent Evaporation of W/O/W Emulsion. *Kagaku Kogaku Ronbunshu* **2000**, 26(1), 81-87.
- 25) Shiomori, K.; Yamada, S.; Baba, Y.; Kawano, Y.; Yoshizawa, H.; Hatate, Y.; Kondo, K. Extraction Equilibrium of Precious Metals with Tri-n-octylamine in Toluene, Proc. The Fourth Japan-Korea Symp. Sep. Tech., **1996**, 367-370.
- 26) Rosenberg, B.; VanCamp, L.; Trosko, J. E.; Mansour, V. H. Platinum Compounds: A New Class of Potent Antitumour Agents. *Nature* **1969**, 222(191), 385-386.
- 27) Kamio, E.; Kondo, K. Separation of Rare Metal Ions by a Column Packed with Microcapsules Containing an Extractant. *Ind. Eng. Chem. Res.* **2002**, 41(15), 3669-3675.

## Figure Captions

- Figure 1** Effect of the chloride ion concentration on the distribution ratios of gold (III) and platinum (IV).
- Figure 2** Breakthrough curves of palladium (III), gold (III), and platinum (IV).
- Figure 3** Effect of flow rate on breakthrough curve of palladium (II).
- Figure 4** Effect of TOA concentration on breakthrough curve of palladium (II).
- Figure 5** Effect of HCl concentration on elution of palladium.
- Figure 6** Elution curves of palladium, gold, and platinum using 8.0 mol/dm<sup>3</sup> HCl aqueous solution.
- Figure 7** Elution curves of gold using 0.1 mol/dm<sup>3</sup> thiourea dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution and 8.0 mol/dm<sup>3</sup> HCl aqueous solution.
- Figure 8** Elution curves of platinum using 0.5 mol/dm<sup>3</sup> ethylenediamine dissolving in 0.1 mol/dm<sup>3</sup> NaOH aqueous solution, 0.1 mol/dm<sup>3</sup> thiourea dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution, 1.0x10<sup>-2</sup> mol/dm<sup>3</sup> NaOH aqueous solution, and 8.0 mol/dm<sup>3</sup> HCl aqueous solution.
- Figure 9** Elution curves of palladium and gold in binary system using 8.0 mol/dm<sup>3</sup> HCl aqueous solution and 0.1 mol/dm<sup>3</sup> thiourea (TU) dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution.
- Figure 10** Elution curves of palladium and platinum in binary system using 8.0 mol/dm<sup>3</sup> HCl aqueous solution and 0.5 mol/dm<sup>3</sup> ethylenediamine (EDA) dissolving in 0.1 mol/dm<sup>3</sup> NaOH aqueous solution.
- Figure 11** Elution curves of palladium, gold and platinum in ternary system using 8.0 mol/dm<sup>3</sup> HCl aqueous solution, 0.1 mol/dm<sup>3</sup> thiourea (TU) dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution, and 0.5 mol/dm<sup>3</sup> ethylenediamine (EDA) dissolving in 0.1 mol/dm<sup>3</sup> NaOH aqueous solution.



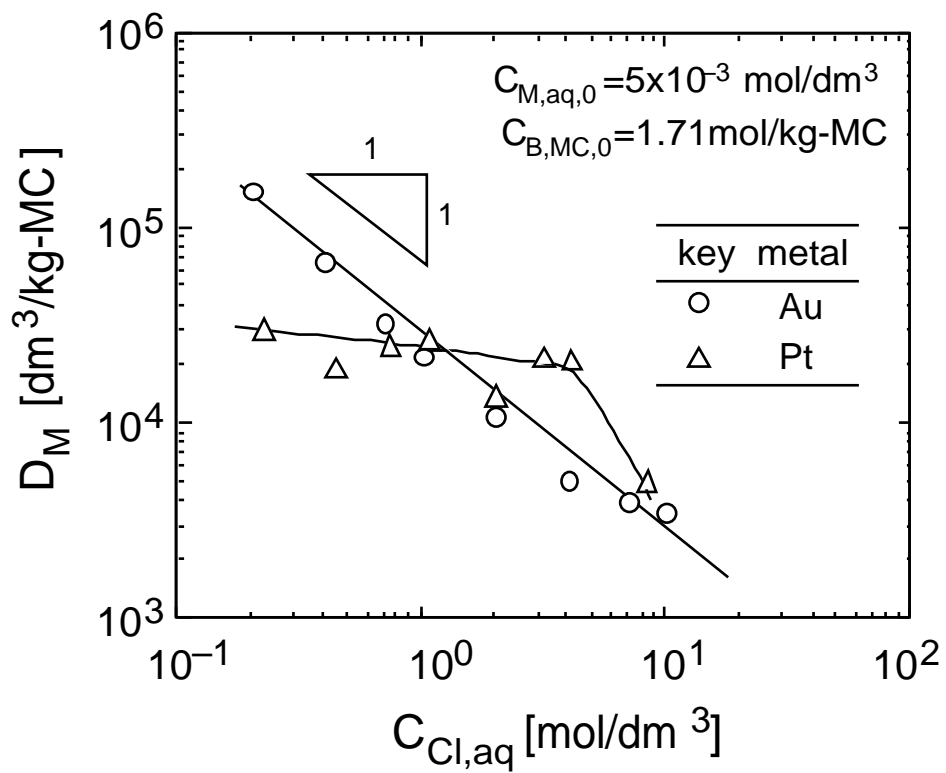


Fig. 1 Effect of the chloride ion concentration on the distribution ratios of gold (III) and palatinum (IV).

H. Yoshizawa et al.

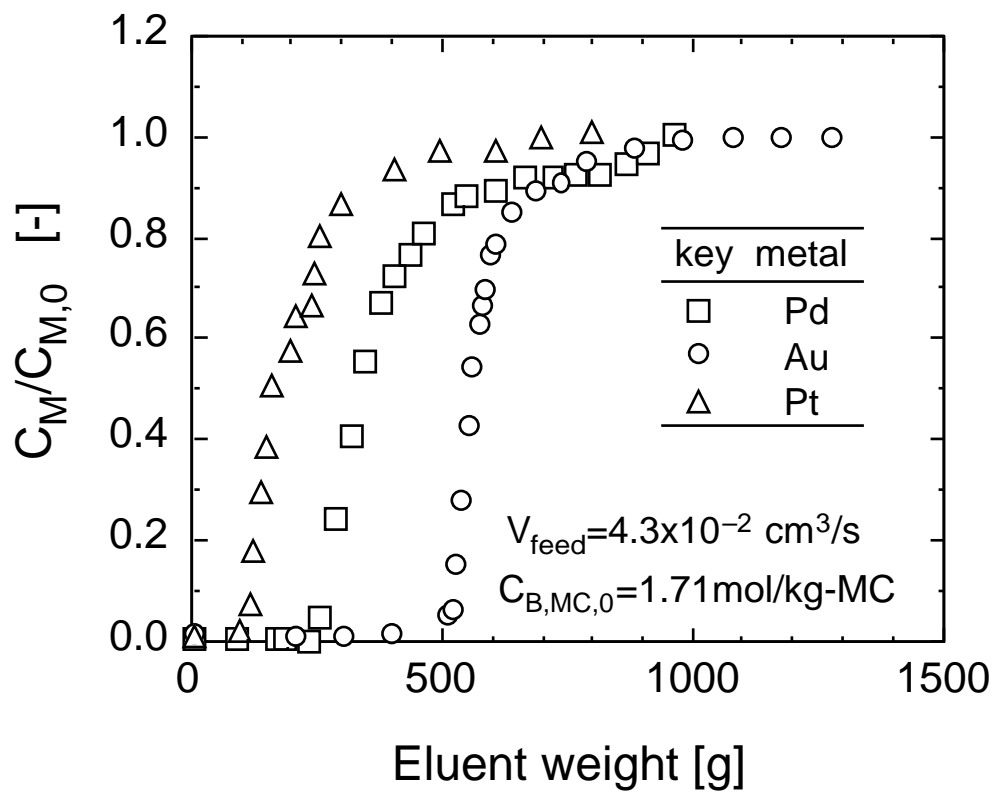


Fig. 2 Breakthrough curves of palladium (III), gold (III), and platinum (IV)

H. Yoshizawa et al.

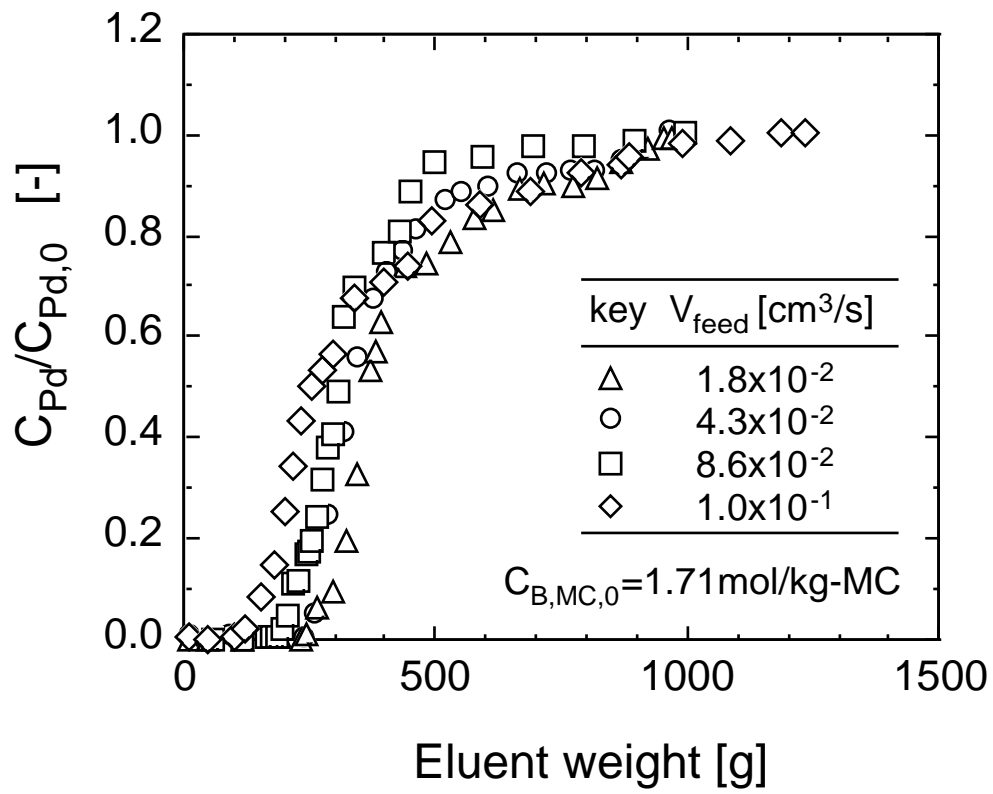


Fig. 3 Effect of flow rate on breakthrough curve of palladium (II).

H. Yoshizawa et al.

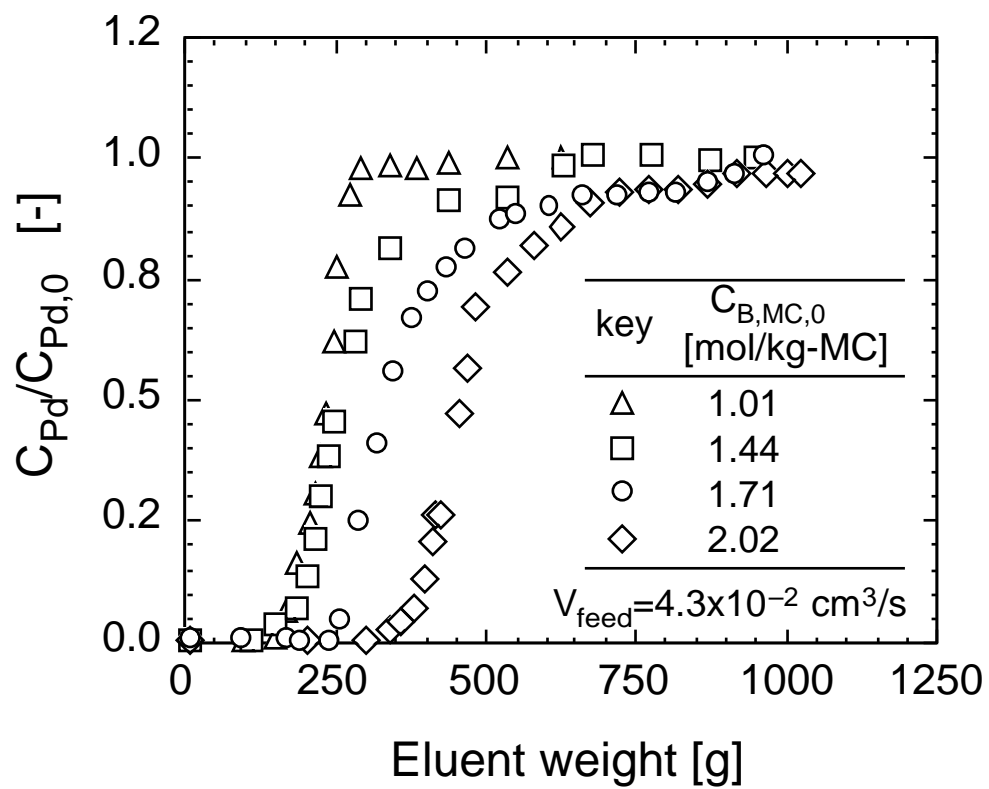


Fig. 4 Effect of TOA concentration on breakthrough curve of palladium (II).

H. Yoshizawa et al.

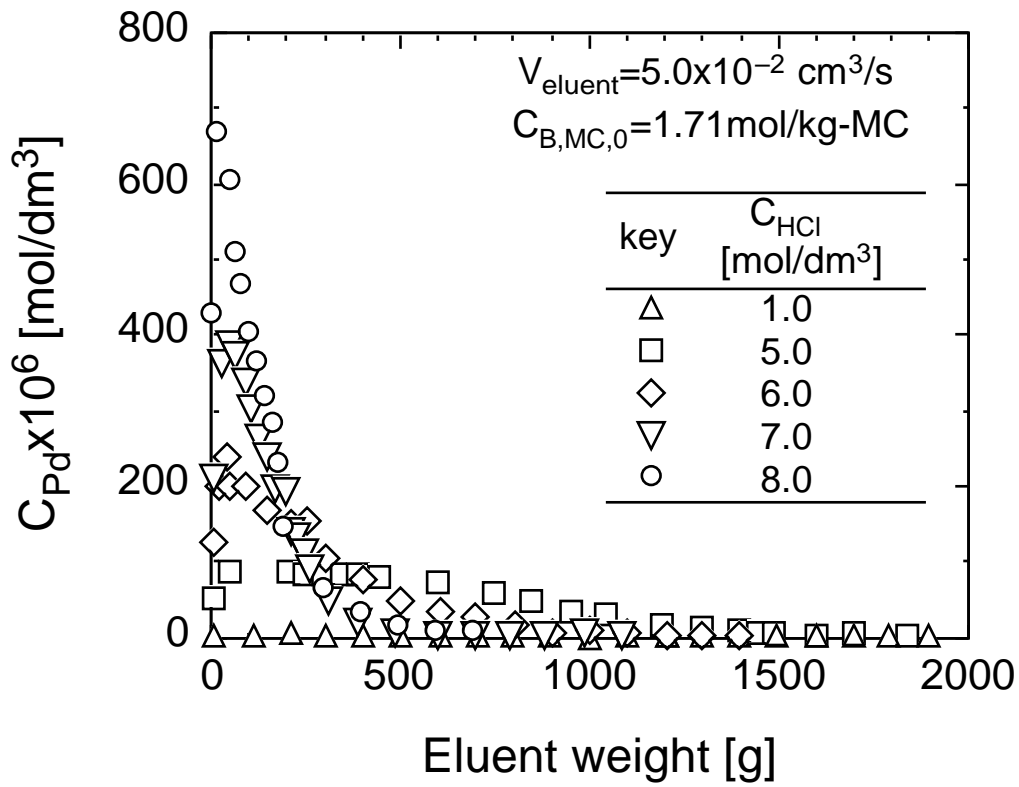


Fig. 5 Effect of HCl concentration on elution of palladium.

H. Yoshizawa et al.

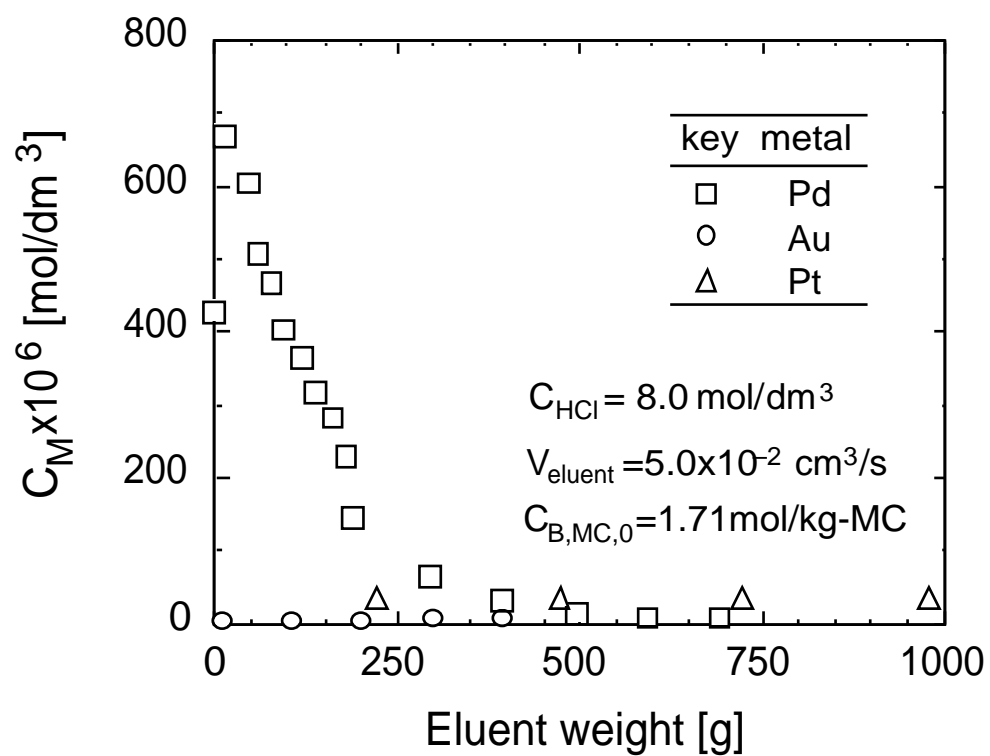


Fig. 6 Elution curves of of palladium, gold, and platinum using  $8.0 \text{ mol/dm}^3$  HCl aqueous solution.

H. Yoshizawa et al.

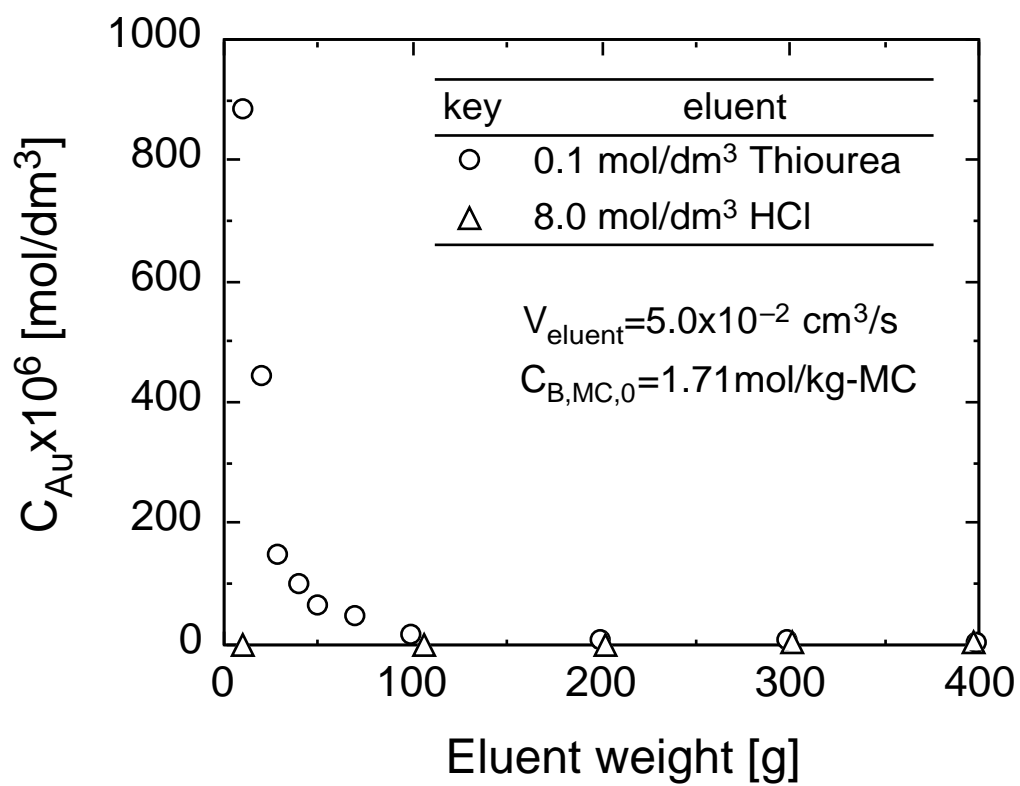


Fig. 7 Elution curves of of gold using 0.1 mol/dm<sup>3</sup> thiourea dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution and 8.0 mol/dm<sup>3</sup> HCl aqueous solution.

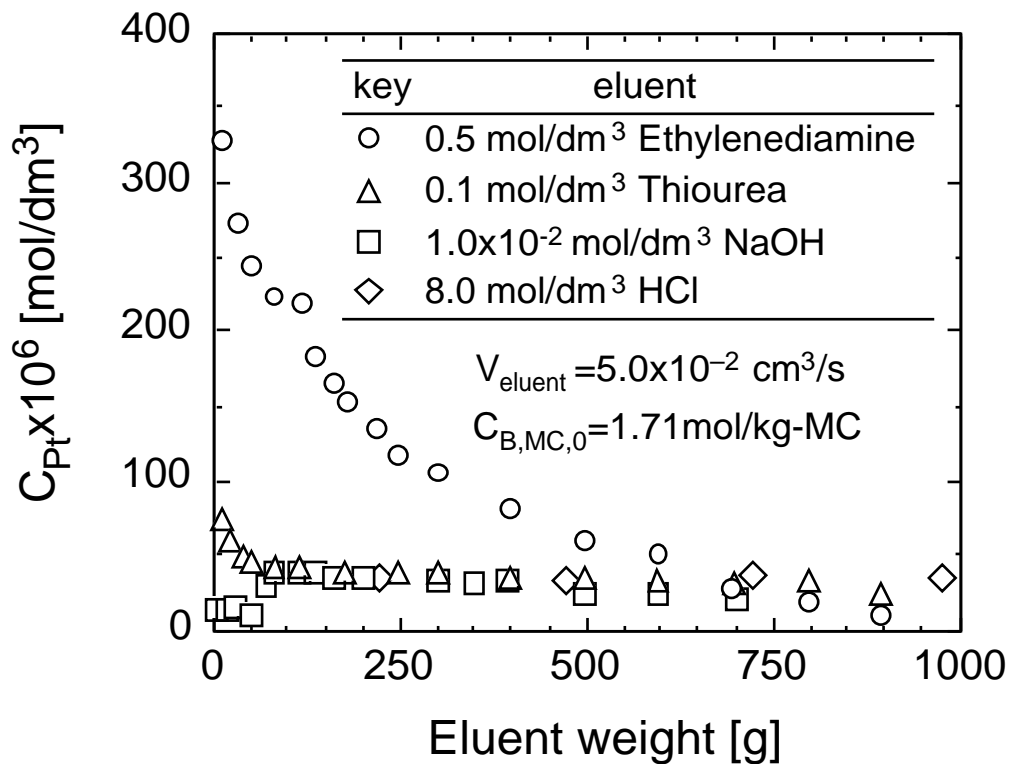


Fig. 8 Elution curves of platinum using 0.5 mol/dm<sup>3</sup> ethylenediamine dissolving in 0.1 mol/dm<sup>3</sup> NaOH aqueous solution, 0.1 mol/dm<sup>3</sup> thiourea dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution, 1.0x10<sup>-2</sup> mol/dm<sup>3</sup> NaOH aqueous solution, and 8.0 mol/dm<sup>3</sup> HCl aqueous solution.

H. Yoshizawa et al.



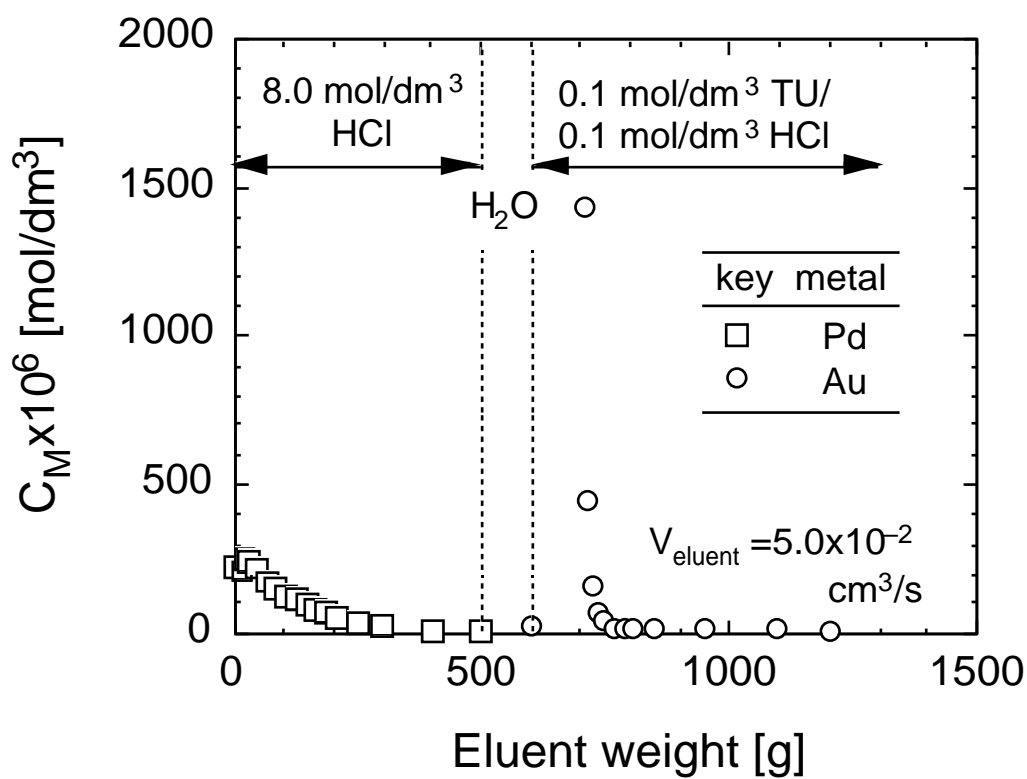


Fig. 9 Elution curves of palladium and gold in binary system using 8.0 mol/dm<sup>3</sup> HCl aqueous solution and 0.1 mol/dm<sup>3</sup> thiourea (TU) dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution.

H. Yoshizawa et al.

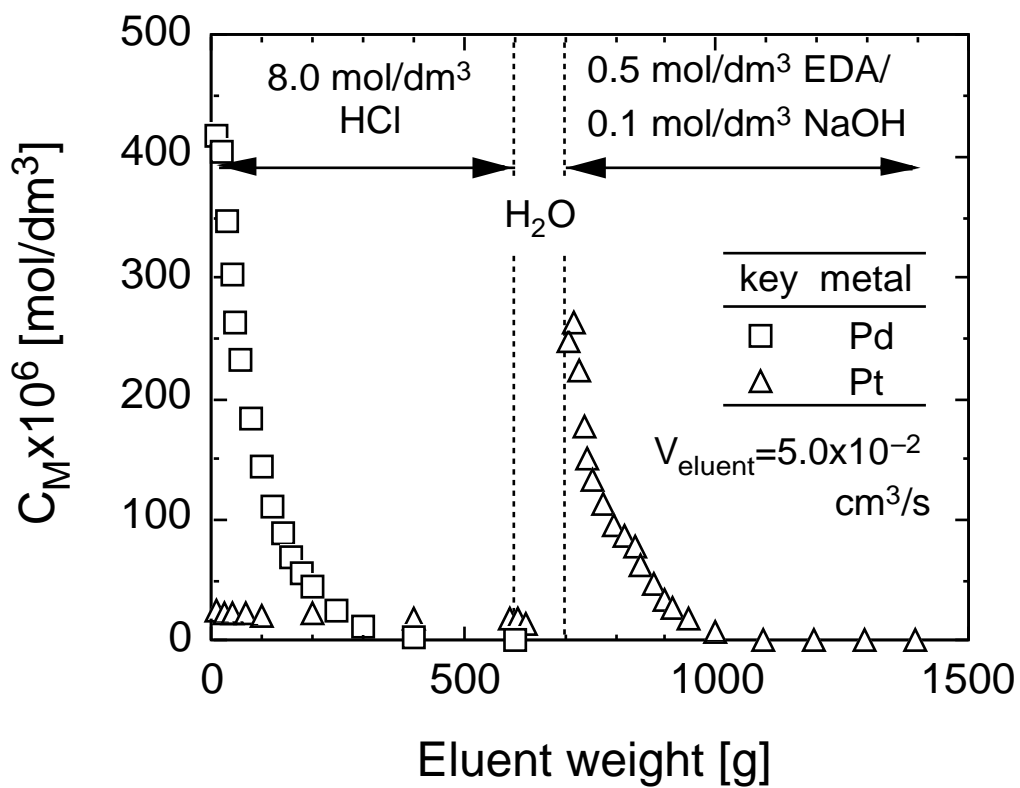


Fig. 10 Elution curves of palladium and platinum in binary system using 8.0 mol/dm<sup>3</sup> HCl aqueous solution and 0.5 mol/dm<sup>3</sup> ethylenediamine (EDA) dissolving in 0.1 mol/dm<sup>3</sup> NaOH aqueous solution

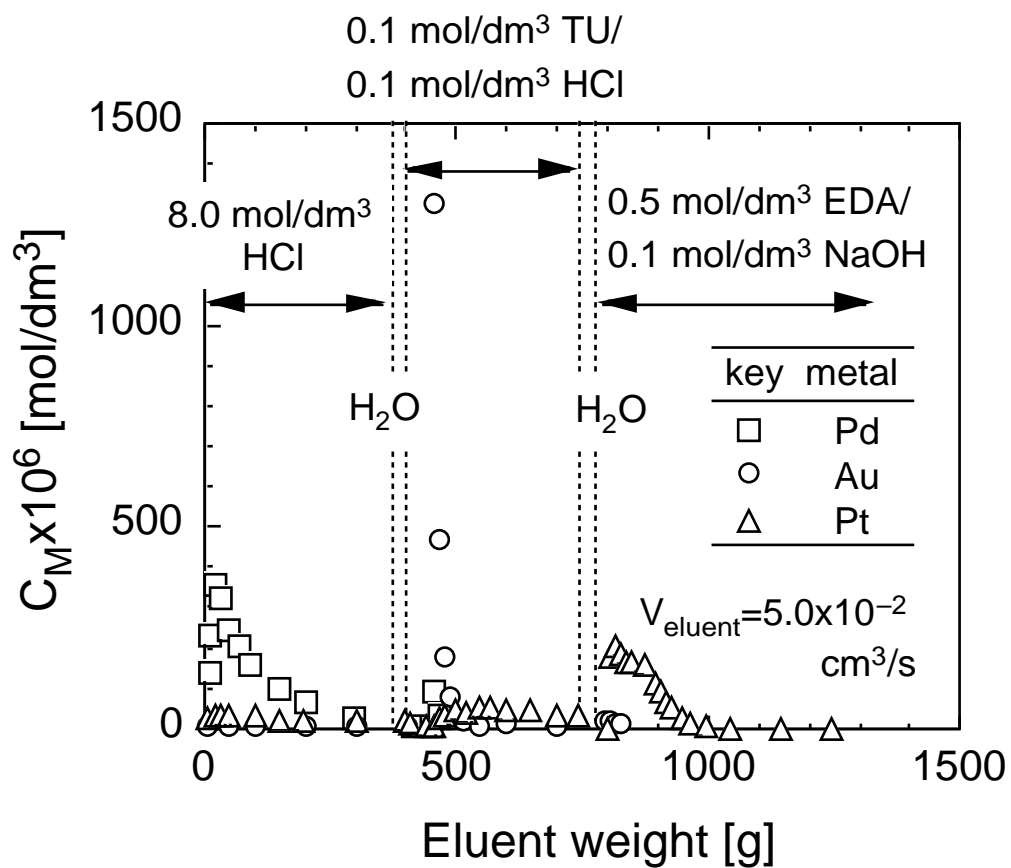


Fig. 11 Elution curves of palladium, gold, and platinum in ternary system using 8.0 mol/dm<sup>3</sup> HCl aqueous solution, 0.1 mol/dm<sup>3</sup> thiourea (TU) dissolving in 0.1 mol/dm<sup>3</sup> HCl aqueous solution, and 0.5 mol/dm<sup>3</sup> ethylenediamine (EDA) dissolving in 0.1 mol/dm<sup>3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

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

	MC-2	MC-3	MC-4	MC-5
Dispersed organic phase				
$C_{\text{DVB}}$ [mol/dm <sup>3</sup> ]	1.60	1.06	2.10	3.15
Core solution	TOA-Toluene	TOA-Toluene	TOA-Toluene	TOA-Toluene
$C_{\text{B}}$ [mol/dm <sup>3</sup> ]	1.14	1.14	1.14	1.14
$\phi$ [-]	0.12	0.12	0.12	0.12
$C_{\text{B,MC}}$ [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, $d_p$ [ $\mu\text{m}$ ]	159	161	197	192

**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 <sup>3</sup> /s]	$C_{M,MC}$ [mol/kg-MC]	Loading ratio [-]
Pd	1.01	2.0	4.9	$4.3 \times 10^{-2}$	0.58	1.1
	1.44	2.0	4.9	$4.3 \times 10^{-2}$	0.72	1.0
	1.71	2.0	4.9	$4.3 \times 10^{-2}$	0.99	1.2
	2.02	2.0	4.9	$4.3 \times 10^{-2}$	1.25	1.2
	1.71	2.0	4.9	$1.8 \times 10^{-2}$	1.09	1.3
	1.71	2.0	4.9	$8.6 \times 10^{-2}$	0.99	0.98
	1.71	2.0	4.9	$1.0 \times 10^{-1}$	0.87	1.0
	1.71	1.0	2.5	$4.3 \times 10^{-2}$	1.08	1.3
	1.71	3.0	7.8	$4.3 \times 10^{-2}$	0.98	1.1
Au	1.71	2.0	4.9	$4.3 \times 10^{-2}$	1.3	0.78
Pt	1.71	2.0	4.9	$4.3 \times 10^{-2}$	0.52	0.61