Separation of a Multitracer from an Au Target Irradiated with High-Energy Heavy Ions by Means of a Supported Liquid Membrane

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The transport of Au(III) and 19 other metal ions through a tributyl phosphate (TBP)-decalin membrane supported on a microporous polytetrafluoroethylene sheet was studied in order to establish a procedure for removing Au(III) ions from acid solutions of a gold target irradiated by high-energy heavy ions, leaving a multitracer solution in a carrier- and salt-free state. Distilled water was used as a stripping agent. A feed solution of 3 mol dm⁻³ HCl gave the highest transport rate in the 0.1–8 mol dm⁻³ HCl range. The transport of carrier-free radioisotopes of Sc, Fe, Zr, Nb, Te, and Hf was observed for 8 mol dm⁻³ HCl and that of Fe, Zr, Nb, and Te for 5 and 6 mol dm⁻³ HCl, while their transport was not detected for 0.1 and 1 mol dm⁻³ HCl feed solutions and was small with 3 mol dm⁻³ HCl. The 3 mol dm⁻³ HCl solution is considered to be the best feed solution for preparing a multitracer from an Au target, because of the large transport rate of Au(III) and the negligible transport of other elements. The transport rates of Au(III) ions from 0.2–2 mol dm⁻³ HNO₃ solutions are smaller than those from 1–6 mol dm⁻³ HCl. On the basis of these observations, a practical procedure was established for preparing a multitracer solution from a heavy-ion-irradiated Au target.

Keywords Supported liquid membrane, TBP-decalin, transport, Au(III), metal ion, multitracer

A large number of radioactive nuclides, useful as tracers, are produced in targets by high-energy heavy-ion irradiation. We demonstrated that the simultaneous use of these tracers provides not only an efficient acquisition of data concerning many elements, but also the acquisition of data under the same experimental conditions.^{1–12} We have been studying how to remove the target materials from acid solutions of the targets while leaving as many types of and as much carrier-free radioactive nuclides as possible in solutions. We previously reported on conventional radiochemical procedures for preparing multitracer solutions from Au, Ag, Cu, and Fe targets irradiated by high-energy heavy-ion beams.^{13–15}

Separation by means of supported liquid membranes is considered to be one of the most useful methods for the removing radioactive nuclides, because: (i) the simplicity of operation, (ii) the feasibility of concentrating radioactive nuclides into a small volume of solution, and (iii) the necessity of a far smaller amount of extractant than in conventional solvent extraction, resulting in little organic radioactive waste. These advantages have promoted extensive applications of the supported liquid-membrane method for separating radioactive elements.^{16–23} Recently, Fu *et al.* reported on the transport of Au(III) ions through a supported liquid membrane impregnated

with trioctylamine.²⁴

We have already briefly reported on the successful removal of the target material Au from acid solutions using a tributyl phosphate (TBP)-decalin membrane.²⁵ Here we describe in detail the transport behavior of not only Au(III) ions, but also various radioactive nuclides produced in the Au target from HCl and HNO₃ feed solutions through a TBP-decalin membrane supported on a microporous polytetrafluoroethylene sheet. Permeation was carried out under various conditions by changing the kind of stripping solution, the concentrations of HCl and HNO₃ in feed solutions and the concentration of TBP in the membrane. TBP was adopted as the carrier in the membrane because Au has the largest distribution coefficient among all of the elements reported for solvent extraction by TBP from 1–12 mol dm⁻³ HCl and 1–3 mol dm⁻³ HNO₃.²⁶

The procedure developed in this work was applied to the actual preparation of a multitracer solution from an Au target irradiated by a 135 MeV/nucleon ¹⁴N beam accelerated by the RIKEN Ring Cyclotron. The merits and demerits of the method are discussed in comparison with other separation methods used in our previous experiments (reduction of Au(III) ions to metal and solvent extraction of Au(III) ions with ethyl acetate).

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Experimental

Preparation of feed solutions

Disks of Au (100 – 300 $\mu\text{m} \times 23 \text{ mm}\phi$) were irradiated by a 135 MeV/nucleon ^{12}C , ^{14}N , or ^{16}O beam accelerated by the RIKEN Ring Cyclotron. An Au target containing various kinds of radioactive nuclides produced by nuclear-fragmentation reactions was dissolved in aqua regia. The solution was evaporated to dryness in a rotary evaporator under reduced pressure. The residue was dissolved in dilute HCl or HNO_3 . HCl (0.1 – 8 mol dm^{-3}) and HNO_3 (0.2 – 2 mol dm^{-3}) containing 10 – 170 mg of Au were used as feed solutions.

Stripping solutions

Distilled water, 0.5 mol dm^{-3} sodium thiocyanate, and 1 mol dm^{-3} sodium bicarbonate solutions were examined as stripping solutions.

Supported liquid membrane

The microporous sheet used as the support for TBP-decalin was polytetrafluoroethylene, Fluoropore FP-045 (Sumitomo Electric Ind.), with an average pore size of 0.45 μm , 75% porosity, and 0.08 mm thickness. A supported liquid membrane with a diameter of 24 mm was prepared by immersing the sheet in TBP-decalin solutions with TBP/decalin ratios of 0.135, 0.27, 1, 2, and 3 for at least 3 d until it became semitransparent. Before use, the sheet impregnated with TBP-decalin was rinsed by dipping it in distilled water with gentle shaking.

Transport and γ -ray measurement

The effect of the TBP concentration of the supported liquid membrane on the transport rate was studied as follows. Each of three supported liquid membranes with different TBP concentrations was fixed at the bottom of a Teflon vessel with a Teflon ring, and 20 cm^3 of distilled water was added to each of these vessels as a stripping solution. The three Teflon vessels were placed in a 3 mol dm^{-3} HCl feed solution (100 cm^3) containing 63.5 mg of gold and radioactive nuclides. The feed solution in the outer vessel was stirred at 1000 rpm using a magnetic stirrer at room temperature. The stripping solutions were stirred by circulating them at a rate of 3 $\text{cm}^3 \text{ min}^{-1}$. Five cubic centimeters of the stripping solutions was withdrawn 0.5 and 1 h after the start of the permeation and subjected to γ -ray measurements. The photopeaks of 355.6 keV γ -rays emitted by ^{196}Au ($T_{1/2} = 6.18 \text{ d}$) were measured with an intrinsic Ge detector.

In the experiment described below, a membrane with a TBP/decalin ratio of 0.27 was used. A Teflon vessel with a membrane at the bottom containing 25 cm^3 of distilled water as a stripping solution was placed in 25 cm^3 of a 3 mol dm^{-3} HCl feed solution containing 10 mg of gold and radioactive nuclides. The feed solution in the outer vessel was stirred at 1000 rpm with a magnetic stirrer at room temperature. The stripping solution was circulated at a rate of 3 $\text{cm}^3 \text{ min}^{-1}$. A

Table 1 Transport rates of Au(III) ions through membranes with TBP/decalin (normalized by the value for the membrane with a TBP/decalin ratio of 1)

TBP/decalin ratio	Relative transport rate
0.135	0.4
0.27	1.0
1	1.0
2	0.8
3	0.9

portion of this circulating solution was trapped in a Teflon vessel set on the top of an intrinsic Ge detector for γ -ray measurements. Measurements of 10 – 20 min duration were automatically repeated for 200 – 300 min, and the obtained γ -ray spectra were recorded on a magnetic disk. After permeation, the γ -ray spectra of all the stripping solutions and feed solutions were measured using the Ge detector for determining the percentage of permeation.

As a stability test of the membrane, permeation was continued for 2 d using 8 mol dm^{-3} HCl and 1 mol dm^{-3} HNO_3 feed solutions containing 170 mg of Au. The stripping solution was replaced with distilled water every time Au(III) transport became saturated.

The transport rates of Au and other carrier-free radioactive nuclides were determined by analyzing the γ -ray spectra on a FACOM M1800 computer at our institute. The nuclides were assigned on the basis of their γ -ray energies and half-lives.

Results and Discussion

Stripping solutions

Distilled water, sodium thiocyanate, and sodium bicarbonate solutions were examined in order to determine the most appropriate stripping solution for our purpose. The transport of Au(III) ions into distilled water proceeded smoothly, while precipitation of metallic Au was observed at the interface between the membrane and the two latter stripping solutions, resulting in a reduction of the transport rate. Therefore, distilled water was used as a stripping solution in the following experiments.

Effect of the TBP concentration on Au(III) transport

Membranes with TBP/decalin ratios of 0.27 – 3 gave no significant difference in terms of the transport rate of Au(III) ions within the limit of the experimental errors, while a membrane with a TBP/decalin ratio of 0.135 showed a smaller transport rate than the former. The results are shown in Table 1. In the experiments described below, membranes with a TBP/decalin ratio of 0.27 were used.

Transport from feed solutions of hydrochloric acid

Figure 1 shows the transport of Au(III) ions from feed

Fig. 1 The transport of Au(III) ions from feed solutions of 0.1 ($\blacktriangle$), 1 ($\circ$), 3 ($+$), 5 ($\square$), 6 ($\triangle$), and 8 ($\bullet$) mol dm⁻³ HCl to distilled water through a membrane with a TBP/decalin ratio of 0.27.

solutions of various concentrations of hydrochloric acid. A feed solution of 3 mol dm⁻³ HCl gave the highest transport rate, though the difference in the initial transport rates was small among the HCl feed solutions in the 1–6 mol dm⁻³ concentration range. More than 90% of the Au(III) ions were transported to the stripping solution within 100 min. On the other hand, the initial transport rates of Au(III) from feed solutions of 0.1 and 8 mol dm⁻³ hydrochloric acid were smaller than those described above, though transport from these two feed solutions was observed to increase with time.

The permeation rate is expressed by

$$\ln[C(t)/C(0)] = -A\varepsilon Pt/V,$$

where $C(t)$ is the concentration of metal ions in the feed solution at time t (in this case, counts), A the geometrical membrane area (cm²), V the volume of the feed solution (cm³), ε the membrane porosity, t the permeation time (s), and P the permeability coefficient (cm s⁻¹). The permeability coefficients of the Au(III) ions were evaluated from the slope of straight lines obtained by plotting the logarithm of the concentration of Au(III) ions in the feed solution, $\ln[C(t)/C(0)]$, vs. the permeation time t . The permeability coefficients were estimated to be about 3×10^{-3} cm s⁻¹ for Au(III) in feed solutions of 1–6 mol dm⁻³ HCl.

The liquid-membrane transport of Au(III) ions by a trioctylamine mobile carrier was studied by Fu *et al.*²⁴ The transport of Au(III) ions from a feed solution of 0.25 mol dm⁻³ HCl to a stripping solution of 1.0 mol dm⁻³ HClO₄ gave the maximum rate constant k , defined by $\ln[C(t)/C(0)] = -kt$. The rate constant is slightly larger than that obtained for feed solutions of 1–6 mol dm⁻³ HCl in this work.

Radioactive nuclides of Sc, Fe, Zr, Nb, Te, and Hf were also found in the stripping solution after 200 min of permeation from a feed solution of 8 mol dm⁻³ HCl. The amounts of transported nuclides decreased along

Table 2 Transport (%) of metal ions from HCl feed solutions

Feed solution (mol dm ⁻³ HCl)	Sc	Fe	Zr	Nb	Te	Hf
0.1	0	0	0	0	0	0
1	0	0	0	0	0	0
3	0	8	0	0	3	1
5	0	100	10	40	30	0
6	1	100	10	60	20	0
8	20	100	30	70	10	5

Fig. 2 Transport of Au(III) ions from feed solutions of 0.2 ($\circ$), 1 ($\triangle$), and 2 ($\square$) mol dm⁻³ HNO₃ to distilled water through a membrane with a TBP/decalin ratio of 0.27.

with a decrease in the acid concentration of the feed solution (Table 2). No radioactivity due to these nuclides was detected for feed solutions of 0.1 and 1 mol dm⁻³ HCl, and only small amounts of Fe, Te, and Hf were transported to the stripping solution from a 3 mol dm⁻³ HCl feed solution. In permeation using feed solutions of 5, 6, and 8 mol dm⁻³ HCl, large amounts of Fe and Nb were removed from the feed solution. Since the 3 mol dm⁻³ HCl feed solution was found to realize a fast elimination of Au(III) ions, and to cause only a small loss in the above-mentioned nuclides during permeation, 3 mol dm⁻³ HCl is concluded to be the most suitable feed solution for preparing a multitracer solution from a gold target.

Transport from nitric acid feed solutions

Figure 2 shows the transport of Au(III) ions from feed solutions of 0.2, 1, and 2 mol dm⁻³ HNO₃ which contained 10 mg of Au. It was found that the acid concentration of the feed solutions only slightly influenced the initial rates of the transport of Au(III) ions; however, the transport reached saturation after 70, 80, and 90% of Au(III) ions had been transported from feed solutions of 2, 1 and 0.2 mol dm⁻³ HNO₃, respectively. The perme-

Fig. 3 Percentage distribution of metal ions in the first (▨), second (■), and third (□) stripping solutions after transport from a feed solution of 8 mol dm⁻³ HCl through a membrane with a TBP/decalin ratio of 0.27 for 30 h.

ability coefficient for Au(III) ions from the solutions was determined to be $7 \times 10^{-4} \text{ cm s}^{-1}$, which is much smaller than that from 1–6 mol dm⁻³ HCl described above. Namely, the transport rates of Au(III) ions from the HNO₃ feed solutions are smaller than those from 1–8 mol dm⁻³ HCl feed solutions. The radioactivities of nuclides other than Au in the stripping solutions were negligible with HNO₃ feed solutions.

Stability of the membranes

In order to estimate the stability of the supported liquid membrane, permeation was performed for a long time using a feed solution of 8 mol dm⁻³ HCl containing 170 mg of Au accompanied by a replacement of the stripping solution with fresh distilled water. Figure 3 shows the percentage distribution of each element in the first, second, and third stripping solutions collected during 0–300, 300–1300, and 1300–1800 min, respectively. Most of the Au(III) ions were found in the first stripping solution and the rest in the second stripping solution. The third stripping solution showed no Au(III) ion color and no Au radioactivity, indicating complete transport of Au(III) ions to the first and second solutions. As described above, in the first stripping solution large fractions of Fe and Nb and small fractions of Sc, Zr, Te, Ce, Hf, and Ir were found. In the second stripping solution, nuclides of Co, Rb, Sr, Y, Rh, Ag, Eu, Gd, Yb, Lu, and Pt were found together with those of Sc, Fe, Zr, Nb, Te, Ce, Hf, and Ir, which were already partly found in the first stripping solution; namely, all of the elements present in the feed solution were found in the second stripping solution. Among them, Te showed a marked increase in the second stripping solution. The fractions of each element transported to the third stripping solution were almost the same as each other. These results suggest that the membrane lost its selectivity at the end of the second permeation stage.

Similarly, permeation from a 1 mol dm⁻³ HNO₃ solution containing 170 mg of Au was carried out by

Fig. 4 Percentage distribution of metal ions in the first (▨), second (■), third (▤), and fourth (□) stripping solutions after transport from a 1 mol dm⁻³ HNO₃ feed solution through a membrane with a TBP/decalin ratio of 0.27 for 46 h.

occasionally replacing the stripping solutions with fresh distilled water. The first stripping solution was collected during 0–340 min, the second during 340–1300 min, the third during 1300–1720 min, and the fourth during 1720–2750 min from the start of permeation. The results are shown in Fig. 4. Complete transport of Au(III) ions was attained after replacing the stripping solution with fresh distilled water three times. The amounts of the other elements, except for Ag, found in the first, second, and third stripping solutions were far smaller than those obtained for the 8 mol dm⁻³ HCl feed solution. About 10% of the nuclides, irrespective of the kind of element, appeared in the fourth stripping solution as a result of membrane deterioration, as in the case of 8 mol dm⁻³ HCl.

These results revealed that the membrane with a TBP/decalin ratio of 0.27 is stable up to about 1000 min for 8 mol dm⁻³ HCl and up to 1700 min for a 1 mol dm⁻³ HNO₃ feed solution.

Preparation of a multitracer solution

On the basis of the experimental results described above, the establishment of a practical procedure for separating a multitracer from an acid solution of an Au target was attempted. About 1 g of an Au target irradiated by a 135 MeV/nucleon ¹⁴N beam was dissolved in aqua regia and evaporated under reduced pressure. The residue was dissolved in 100 cm³ of 3 mol dm⁻³ HCl. The solution was transferred to a compartment of an apparatus (Fig. 5) which had two Teflon compartments (80 mmϕ×25 mm) separated by a supported liquid membrane containing a one-to-one TBP/decalin solution. One hundred cubic centimeters of distilled water was filled as a stripping solution in the other compartment. Each solution was stirred by circulation with microtube pumps at a rate of 3 cm³ min⁻¹. About 50% of the Au(III) ions were transported to distilled water 3 h after the start of permeation; the

Fig. 5 Permeation apparatus.

transport increased to 90, 95, and 98% after 19, 26, and 45 h permeations, respectively, showing signs of saturation at the end. The complete removal of Au(III) ions was observed 6 h after replacing the stripping solution with fresh distilled water.

As described above, Au(III) ions can be transported from both HCl and HNO₃ feed solutions. Therefore, permeation from an aqua-regia solution was examined as the final practical procedure. In this case, 4.8 g of Au target was dissolved in 20 cm³ of aqua regia. This solution was used for permeation after dilution with distilled water to 100 cm³. In order to avoid saturation, permeation was carried out with a continuous supply of fresh distilled water to the stripping-solution compartment at a rate of 2 cm³ min⁻¹. Aliquots of the feed solution were withdrawn and the radioactivity of Au* was measured using a Ge detector. Figure 6 shows the decrease of Au* in the feed solution with the permeation time. About 99% of the Au(III) ions were removed from the feed solution within 70 h. Only peaks due to Au* were detected in the stripping solution, showing selective permeation of the Au(III) ions.

The procedures for preparing the multitracer used in our previous work were: (i) filtration of Au metal after the reduction of Au(III) ions with H₂O₂, leaving the multitracer in the filtrate and (ii) ethyl acetate extraction of Au(III) from a 3 mol dm⁻³ HCl solution. Both methods have both merits and demerits. Since H₂O₂ reduces only Au(III) ions to metal, radioactive nuclides of all the elements produced in the Au target remain in the filtrate. However, it requires a lot of time to completely reduce Au(III) ions, because a trace amount of HNO₃ in the residue after the evaporation of aqua regia hinders the reduction of Au(III). Therefore, evaporation of the target solution and reduction of Au(III) with H₂O₂ must be repeated several times to ensure complete removal of Au(III) from the solution. Although solvent extraction of Au(III) ions with ethyl acetate is a rapid method, some Fe, Te, Re, and Hg are coextracted into the organic phase.

The method of separating Au(III) ions by means of the supported liquid membrane developed in the present work requires about 3 d for an Au target of about 5 g,

Fig. 6 Transport of Au(III) ions (4.8 g) from a feed solution of 1.8 mol dm⁻³ in HCl and 0.7 mol dm⁻³ in HNO₃ to distilled water through a membrane with a TBP/decalin ratio of 1.

which is comparable to the time required for the reduction with H₂O₂. However, once the experimental setup is ready for permeation, the transport of Au(III) ions proceeds automatically. Therefore, this method can reduce the workload as well as the radiation exposure dose to researchers. The separation time will be considerably shortened by using a membrane with a large surface area, such as a hollow fiber module.

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