

Development of On-line Solvent Extraction System with Microchips for Heavy Element Chemistry

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A technique of microchip chemistry was introduced into an on-line solvent extraction system for studies of chemical behaviors of heavy elements, and the performance of the system was investigated with some rare earth elements as their homologues. It was confirmed that the extraction equilibria of the elements between the aqueous (acetic acid-sodium acetate buffer solution) and organic (2-thenoyltrifluoroacetone-toluene solution) phases were attained in the microchip within about one second. Using the system, on-line solvent extraction experiments were performed for the short-lived ^{150,151}Dy as model experiments of heavy actinides at the AVF cyclotron facility of the Research Center for Nuclear Physics (RCNP), Osaka University. All the chemical stages from the RI production to their detections were completed within about three minutes, signifying that this system is applicable to studies of heavy actinides having half-lives of a few minutes.

1. Introduction

Investigation of the chemical properties of the heavy elements with atomic numbers ≥ 101 is an attractive subject because the chemical properties of the heavy elements may deviate from the periodicity of their lighter homologues in the Periodic Table as theoretically predicted as to the strong relativistic effects on their valence electrons.^{1,2} The heavy elements can be produced only in heavy-ion induced nuclear reactions using an accelerator. Because of their low production rates and short half-lives, the chemistry of these elements has to be performed on a single atom basis (one-atom-at-a-time chemistry^{3,4}), and on-line rapid chemical operations are required.^{1,2} For these purposes, much effort has been made in the research and development, and some rapid chemical operation systems have already been in practical use: a liquid chromatographic separation system called ARCA⁵ and a solvent extraction system called SISAK,⁶ for example. As has been performed in experiments with SISAK, the solvent extraction method is useful for investigation on the chemical properties of heavy elements because we can obtain the equilibrium constants of complexation reactions, which provide information about the chemical bonding nature of the complexes.

In the present work, we incorporated microchips in a solvent extraction system for their application to heavy element chemistry as a simple method. Microchips⁷⁻⁹ are glass plates utilized for chemical reactions, having microscale ditches of typically 1–100 μm in width and depth. Because of a large specific interfacial area and a short diffusion length of solutes, chemical equilibria are rapidly achieved in the microspace, which is very much suited to heavy element chemistry. Using the present system, we examined solvent extraction behaviors of the rare earth elements: Y, Gd, Tm, and Dy; as test experiments for the homologues of heavy actinides. In this paper, the performance and applicability of the present on-line solvent extraction system are shown.

2. Experiments

2.1. Experimental apparatus. The on-line solvent extraction system was installed at the AVF cyclotron facility of the Research Center for Nuclear Physics (RCNP), Osaka University. As schematically depicted in Figure 1, the system consists of two different parts: a production chamber for heavy elements and a solvent extraction apparatus with microchips. They are connected with a gas-jet transport system. The specifications of each part of the system are shown in the following subsections.

2.1.1. Production chamber for heavy elements. We newly installed a production chamber for heavy element chemistry at the K-course of the AVF cyclotron of RCNP. The structure of the production chamber is similar to that used in the Japan Atomic Energy Agency (JAEA),¹⁰ having a size of 55 mm i.d. \times 49 mm. The size of reaction targets is 9 mm in diameter. The heavy-ion beam passes through several different materials

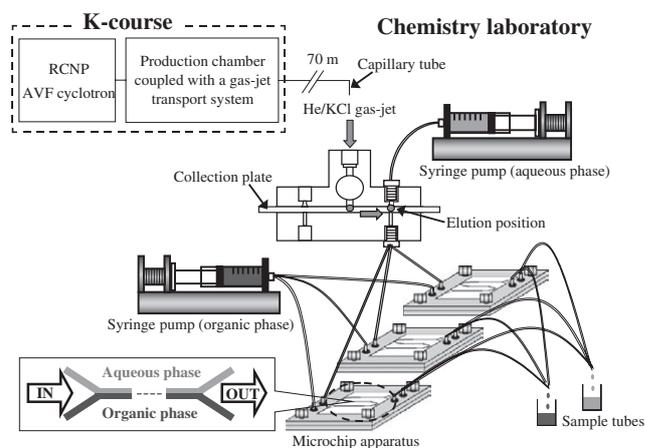


Figure 1. Schematic view of the on-line solvent extraction system installed at the AVF cyclotron facility of RCNP. The system consists of a production chamber for heavy elements and a solvent extraction apparatus with microchips. They are connected with a gas-jet transport system. The structure of the production chamber is similar to that used in the Japan Atomic Energy Agency (JAEA).¹⁰

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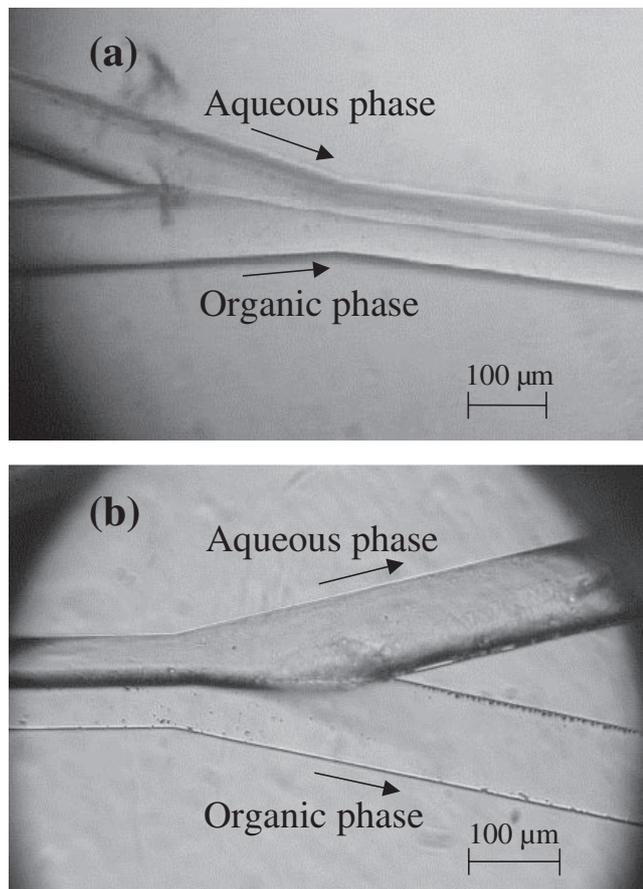


Figure 2. Photographs of the liquid-liquid interface and phase separation (a) at the inlet junction and (b) at the outlet junction of the microchannel in a microchip.

before the target for nuclear reactions: a beam current monitor consisting of three aluminum foils (4.8 mg cm^{-2} in total) coated with gold (0.81 mg cm^{-2} in total), a HAVAR vacuum window (4.4 mg cm^{-2}), helium cooling gas (0.41 mg cm^{-2}), two HAVAR vacuum windows (8.8 mg cm^{-2} in total), helium cooling gas (0.06 mg cm^{-2}), and a target backing. Reaction products recoiling out of the target are thermalized in a helium gas flow, attached to KCl aerosols generated by sublimation of KCl powder, and then transported through a Teflon capillary (2 mm i.d. \times 70 m) to the on-line solvent extraction apparatus placed in a chemistry laboratory. The transport efficiency of reaction products is approximately 35%.

2.1.2. On-line solvent extraction apparatus. Nuclear reaction products transported by the gas-jet are kept deposited on a collection plate. The collected products are mechanically moved to the elution position and then dissolved in an aqueous solution pumped by a syringe pump (HARVARD, PHD2000). The yield by the dissolution is approximately 60%. The dissolved products are fed into a microchip apparatus through a polyether ether ketone (PEEK) capillary (0.26 mm i.d., 0.5 mm o.d.). Simultaneously, the organic phase is fed from the other inlet of the microchip (Institute of Microchemical Technology Co. Ltd., ICC-DY15). The sectional view of the flow channel in the microchip (called a microchannel hereafter) is a half circle of $100 \mu\text{m}$ in width and $40 \mu\text{m}$ in depth. The microchannel is 12 cm long. The wall of the microchannel for the organic phase is chemically modified so as to be hydrophobic.¹¹ In the microchannel of the microchip, a parallel two-phase flow with a liquid-liquid interface is formed. At the end-junction of the microchannel, two phases are separated without mixing with each other as shown in Figure 2. The aqueous and organic effluents coming out of the microchip are collected separately in sample tubes. Because the volume of the solution treated in a single microchip is minute, we employed a multi-track micro-

chip system composed of three microchips arranged in parallel in order to increase the volume of the solution treated per unit time in the microchip apparatus. In this apparatus, an aqueous solution of about $50 \mu\text{L}$ is needed to dissolve all collected radioactivities when the flow rate of the solution is $50 \mu\text{L min}^{-1}$. The volume of PEEK capillaries connected to the multi-track microchip is about $50 \mu\text{L}$ and the total volume of microchannels for either phase is about $1 \mu\text{L}$.

2.2. Extraction equilibrium in a microchip. It is important to investigate the reaction time required to attain the extraction equilibrium in the microchip. The contact time of the aqueous and organic phases in a microchip corresponds to the shaking time for the ordinary batch method. Therefore, we examined the contact time of the liquid-liquid interface required to attain the equilibrium by varying the flow rates of both the solutions. In addition, batch experiments were performed to examine if the extraction percentage in the microchip experiments would agree with that in the ordinary solvent extraction experiments.

The rare earth tracers as the homologues of heavy actinides were prepared by different nuclear reactions. The ^{88}Y tracer was obtained from the EC decay of ^{88}Zr produced by the $^{89}\text{Y}(p,2n)^{88}\text{Zr}$ reaction and the ^{153}Gd tracer by the $^{153}\text{Eu}(p,n)^{153}\text{Gd}$ reaction with the AVF cyclotron of RCNP. The ^{170}Tm tracer was produced by neutron irradiation of Tm_2O_3 at Kyoto University Reactor. The aqueous phase used was 0.1 M acetic acid-sodium acetate buffer (pH 4.5) containing the tracers, and for the organic phase 0.04 M 2-thenoyltrifluoroacetone (HTTA)-toluene solution was employed.¹² The aqueous and organic phases were simultaneously fed into each of the inlets of a microchip with syringe pumps. The flow rate was varied in the range from $3 \mu\text{L min}^{-1}$ to $120 \mu\text{L min}^{-1}$. The aqueous and organic effluents from the microchip were collected separately in sample tubes, and were subjected to γ -ray spectrometry with a Ge detector.

The batch experiments were performed by the following procedure. In a polypropylene tube, 1 mL of 0.1 M acetic acid-sodium acetate buffer (pH 4.5) containing the above tracers was mixed with an equal volume of 0.04 M HTTA-toluene solution. The mixture was shaken for 20 min. After centrifuging, the aliquots of the aqueous and organic phases were recovered separately in sample tubes, and subjected to γ -ray spectrometry.

2.3. On-line experiments using the solvent extraction system. The short-lived dysprosium isotopes, ^{150}Dy ($T_{1/2} = 7.17 \text{ min}$) and ^{151}Dy ($T_{1/2} = 17.9 \text{ min}$) were produced by the $^{140}\text{Ce}(^{16}\text{O},6n)^{150}\text{Dy}$ and $^{140}\text{Ce}(^{16}\text{O},5n)^{151}\text{Dy}$ reactions¹³ with a 102 MeV ^{16}O beam delivered from the K course of the AVF cyclotron of RCNP. The ^{nat}Ce target of a thickness of $211 \mu\text{g cm}^{-2}$ was in advance prepared by electrodeposition on a 2.7 mg cm^{-2} aluminium backing foil. The beam intensity was approximately 160 particle nA. Reaction products recoiling out of the target were thermalized in a helium gas flow (2.5 L min^{-1} , 178 kPa in the production chamber), attached to KCl aerosols generated by sublimation of KCl powder at 620–640 $^\circ\text{C}$, and then transported to the chemistry laboratory. The transported products were kept deposited on the collection plate for five minutes, dissolved in dilute hydrochloric acids (pH 3.01, 3.14, 3.23, 3.40) pumped by a syringe pump at a flow rate of $50 \mu\text{L min}^{-1}$, and subsequently fed into the multi-track microchips. A toluene solution of 0.1 M HTTA was fed from the other inlets with a syringe pump at a flow rate of $90 \mu\text{L min}^{-1}$. The aqueous and organic effluents from the microchip were collected separately on Ta discs. After evaporation to dryness on ceramic heaters, the samples were subjected to α spectrometry with Si detectors. The distribution ratio was obtained from the activities of these two phases.

3. Results and Discussion

3.1. Extraction percentage. The dependences of the extraction percentages of the rare earth elements on the contact time of the liquid-liquid interface in the microchip are shown in Figure 3. The three different lines stand for the extraction percentages of each rare earth element obtained in the batch experiments. The extraction percentage (P) is defined as

$$P = \frac{100A_oV_a}{A_oV_a + A_aV_o} = \frac{100A_o v_a t}{A_o v_a t + A_a v_o t} = \frac{100A_o v_a}{A_o v_a + A_a v_o}, \quad (1)$$

where A is the radioactivity, V the volume, v the flow rate, and t the collection time of the aqueous and organic effluents. The subscripts a and o denote the aqueous and organic phases, respectively. The contact time is calculated from the flow rate of a faster phase and the volume of the microchannel where two phases contact. One can see in Figure 3 that the extraction percentages of the rare earth elements increase with the contact time, and reach the values obtained by the batch method after one second. These results evidently show that the microchip is applicable to rapid chemistry for the heavy elements having half-lives of a few seconds.

3.2. On-line solvent extraction of dysprosium. The distribution ratio (D) is defined as

$$D = \frac{A_o V_a}{A_a V_o} = \frac{A_o v_a t}{A_a v_o t} = \frac{A_o v_a}{A_a v_o}. \quad (2)$$

Here, A_a and A_o were obtained from the α counts of ^{150}Dy ($E_\alpha = 4233$ keV) and ^{151}Dy ($E_\alpha = 4067$ keV). An example of α -particle spectra of ^{150}Dy and ^{151}Dy obtained from this experiment (pH 3.14) is shown in Figure 4. The α -particle energy resolution in the organic phase was about 40 keV in FWHM, whereas for the aqueous phase, the resolution was poor because of the KCl residues from the gas-jet. This was not a serious problem with determining the quantities of Dy because no events other than Dy were observed in these experiments. The dependence of the distribution ratio of Dy on pH is shown in Figure 5. The extraction of trivalent lanthanides (Ln^{3+}) by HTTA is usually

described by the following reaction:¹⁴



The extraction equilibrium constant (K) is expressed for the

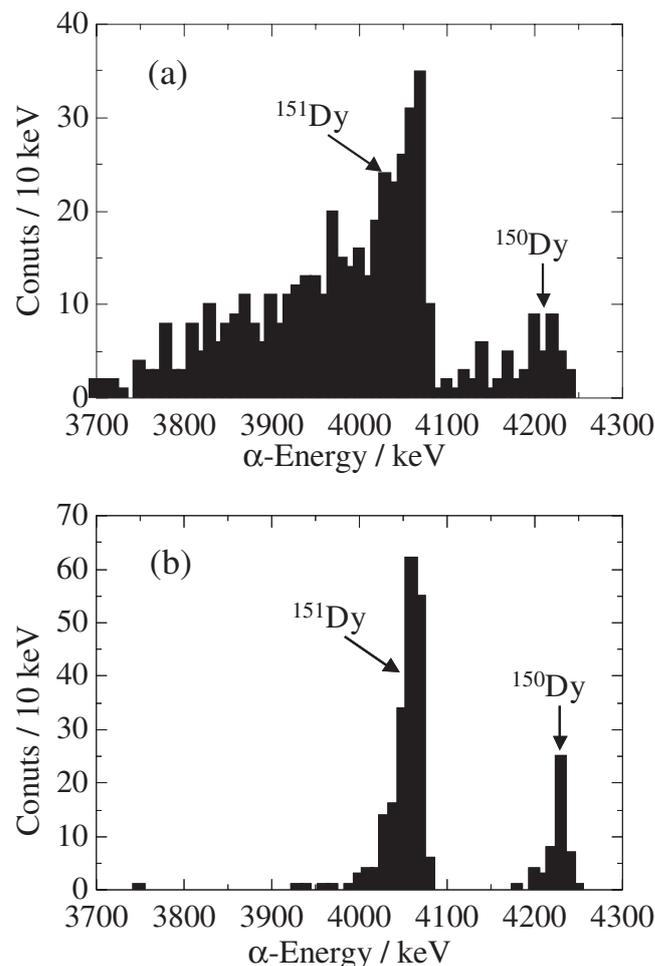


Figure 4. Alpha-particle spectra, obtained by the on-line experiment of ^{150}Dy and ^{151}Dy , (a) for the aqueous phase (hydrochloric acid of pH 3.14) and (b) for the organic phase (0.1 M HTTA-toluene solution).

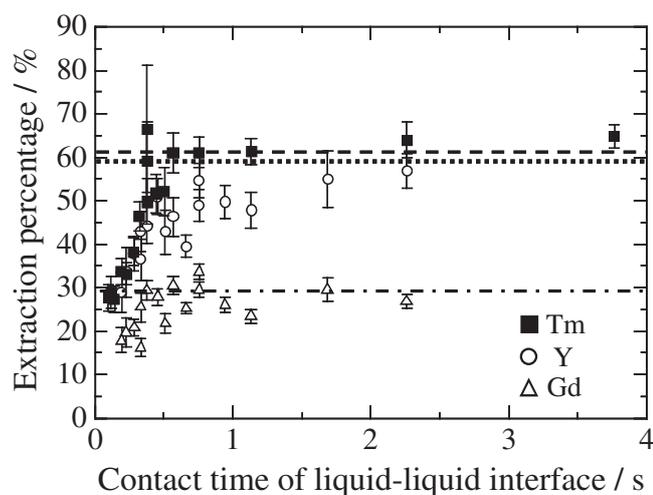


Figure 3. Dependences of the extraction percentages of rare earth elements on the contact time of the liquid-liquid interface in the microchip. For the aqueous and organic phases, 0.1 M acetic acid-sodium acetate buffer (pH 4.5) and 0.04 M HTTA-toluene solution were used, respectively. The closed square, the open circle, and the open triangle symbolize Tm, Y, and Gd, respectively. The lines show the extraction percentages of each rare earth element obtained by the batch experiments. The dashed line, the dotted line, and the dashed-dotted line correspond to Tm, Y, and Gd, respectively.

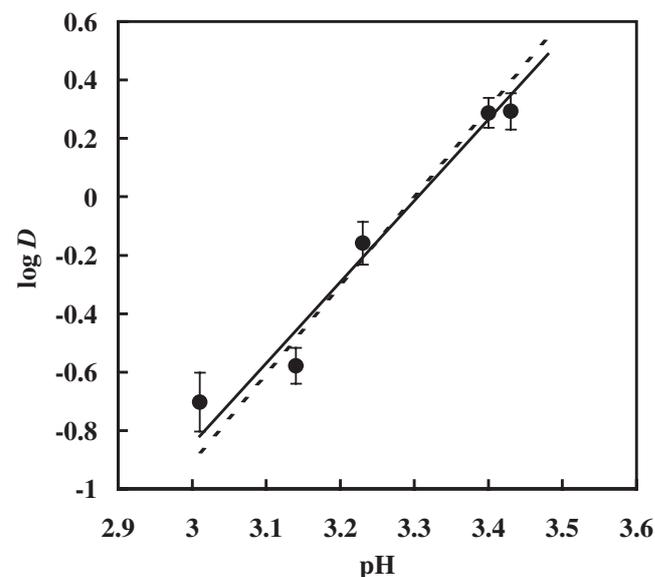


Figure 5. Distribution ratio of Dy as a function of pH taken with the on-line solvent extraction system. For the organic phase, 0.1 M HTTA-toluene solution was used. The solid line of a slope of 2.78 ± 0.20 was obtained from a weighted least-squares fit to the experimental values. The dashed line shows the result of another least-squares fit with the slope fixed to 3. See the text for detailed explanations.

reaction as:

$$K = \frac{[\text{Ln}(\text{TТА})_3]_{(o)}[\text{H}^+]^3}{[\text{Ln}^{3+}][\text{HTТА}]_{(o)}^3} \quad (4)$$

The distribution ratio is also defined as

$$D = \frac{[\text{Ln}(\text{TТА})_3]_{(o)}}{[\text{Ln}^{3+}] + [\text{Ln}(\text{TТА})_2^+] + [\text{Ln}(\text{TТА})_2^+] + [\text{Ln}(\text{TТА})_3]} \quad (5)$$

Neglecting the metal complexes in the aqueous phase ($[\text{Ln}(\text{TТА})_2^+]$, $[\text{Ln}(\text{TТА})_2^+]$, and $[\text{Ln}(\text{TТА})_3]$), we can simplify eq 4 as

$$K = D \frac{[\text{H}^+]^3}{[\text{HTТА}]_{(o)}^3} \quad (6)$$

Equation 6 means that $\log D$ vs. pH plots give a linear plot with a slope of 3, which is confirmed by solvent extraction experiments of rare earth elements with HTТА.¹⁴ As shown in Figure 5, the slope was estimated to be 2.78 ± 0.20 by a weighted least-squares fit to the experimental values. Taking into account the uncertainty, this result can be regarded as reproducing the above report.¹⁴ The reproducibility is also confirmed from the fact that another least-squares fitting process with the slope fixed to 3 passes the chi square test with a confidence coefficient of 95% (see the dashed line in Figure 5). We therefore concluded that this system functioned well in the extraction of Dy.

It took only about three minutes to complete the sample preparations for α -particle measurements starting from the beginning of dissolution: one minute for the dissolution, one minute for the elution from the apparatus, and one minute for the sample preparations for the α -particle measurement. It was hence found that this system can be applied to the solvent extraction experiments of the heavy actinides having half-lives of a few minutes.

To utilize the short reaction time of one second in the microchip, the following improvements of the apparatus are needed: (1) introduction of a PEEK capillary with a smaller inner diameter for the decrease of the dead volume in the apparatus and (2) additional parallelization of microchips for the increase of the volume of the solution treated per unit time in the microchip apparatus. Furthermore, automation of the experimental procedure from the solvent extraction to the radiation detection is essential for repetitive experiments in the chemistry of transactinide elements.

4. Conclusion

An on-line solvent extraction system with microchips for heavy element chemistry was installed in the AVF cyclotron facility of RCNP. The extraction equilibria of the rare earth elements, Y, Gd, and Tm, between acetic acid-sodium acetate buffer solution and HTТА-toluene solution were attained within about one second in the microchip. The extraction percentages of the rare earth elements at the equilibria obtained by the microchip method agreed with those obtained by the batch method. These results evidently show that the microchip is applicable to rapid chemistry for the short-lived elements of

half-lives having a few seconds. On-line solvent extraction experiments of Dy using the system were successfully performed. The total time taken for the on-line experiments was about three minutes. This system can thus be used for the solvent extraction experiments of the heavy actinides having half-lives of a few minutes.

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