Chelate extraction of zirconium and hafnium using flow injection analysis technique for aqueous chemistry of element 104, rutherfordium

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We have been investigating the solvent extraction behavior of Zr and Hf, which are lighter homologues of rutherfordium (Rf, element 104), with chelating agents 2-thenoyltrifluoroacetone (HTTA) and di(2-ethylhexyl)phosphoric acid (HDEHP). In our previous study, the extraction mechanisms of Zr and Hf with TTA[1] and HDEHP[2] from 3 M acid solution were investigated using the batch method. The plots of the logarithm of distribution ratio (D) of Zr and Hf ($\log D$) against $\log$ [TTA or (HDEHP)$_2$] showed a linear relation with a slope of approximately 4, suggesting that the extraction species of Zr and Hf were M(TTA)$_4$ or M(HDEHP·DEHP)$_4$ (M = Zr or Hf). However, it took about tens of minutes to several hours to reach extraction equilibrium with these chelating agents. For extraction studies with a short-lived Rf isotope, more rapid extraction is required. In our previous study,[3] rapid extraction equilibrium was attained using a flow injection analysis (FIA) technique for the extraction of ^{95g}Nb from hydrochloric acid into Aliquat 336/1,2-dichloroethane. In this study, we applied this rapid solvent extraction apparatus for Zr and Hf extraction with HDEHP.

Radiotracers of ^{88}Zr ($T_{1/2} = 83.4$ d) and ^{175}Hf ($T_{1/2} = 70$ d) were produced in the bombardment of metallic ^{89}Y and ^{nat}Lu foils, respectively, with a 24-MeV deuteron beam from the RIKEN K70 AVF cyclotron. These radiotracers were chemically separated from the target materials through anion exchange and the solvent extraction method. A schematic view of the FIA apparatus used in this study is shown in Fig. 1. Three molar concentrations of perchloric acid containing the tracers and 1.5×10^{-3} M HDEHP in toluene were used as aqueous and organic phases, respectively. These solutions were pumped with double-plunger pumps at the same flow rate of 0.10 or 0.50 mL min^{-1} and mixed in the extraction coil (Teflon capillary) with an inner diameter of 0.17 mm. The length of the extraction coil was changed from 0.5 to 10 m to vary the contact time of the two phases. The aqueous and organic solutions eluting from the extraction coil were collected in a sample tube, which was subsequently centrifuged. The aliquots of these two phases were separately pipetted into other sample tubes and subjected to γ-ray spectrometry using a Ge detector. Because the flow rate of the aqueous phase was the same as that of the organic phase, the D values of Zr and Hf were evaluated from the following simple equation:

$$D = A_o/A_a,$$

where A denotes the radioactivity of either ^{88}Zr or ^{175}Hf, and the subscripts a and o refer to the aqueous and organic phases, respectively.

Figure 2 shows the dependences of the D values of Zr and Hf on the contact time of the two phases in the extraction coil. The results obtained with the batch extraction method are also shown in Fig. 2. The dashed and solid lines in the figure show the D values of Zr and Hf, respectively, at the extraction equilibrium. The D values of Zr and Hf obtained with the FIA apparatus increase more rapidly than those obtained in the batch extraction, showing that the extraction reaction was enhanced by the FIA apparatus. However, extraction equilibrium was not attained with the FIA apparatus within the contact time of approximately 1 min, which corresponded to the half-life of ^{261}Rf ($T_{1/2} = 68$ s). Therefore, further enhancement of the extraction reaction through heating or vigorous agitation of the two phases in the extraction coil is required.
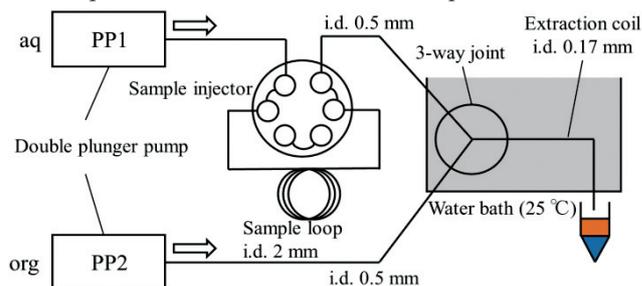
Fig. 1. Schematic view of the FIA apparatus setup.
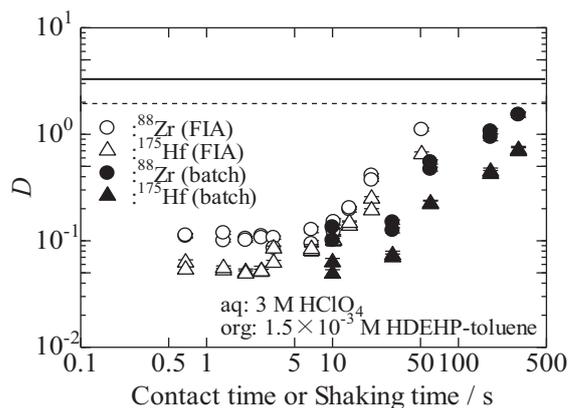
Fig. 2. Dependences of the D values of ^{88}Zr and ^{175}Hf on the contact time in the FIA apparatus or shaking time in the batch experiment. The dashed and solid line indicate the D values of ^{88}Zr and ^{175}Hf at equilibrium, respectively.

References
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