Adsorption behavior of Zr and Hf to TTA-resin in microcolumn for determining the forming ability of Rf monofluoride complex

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The present study aims to elucidate the relevant chemical species of Rf by reversed-phase extraction chromatography with 2-thenoyltrifluoroacetone (TTA) as a stationary phase. Because TTA has been suggested to extract quadrivalent metallic ions, the distribution ratios of the system may make it possible to determine the specific complex-formation constant of Rf. We have so far performed several experiments for the chemical systems with Zr and Hf ions, but failed to find an experimental condition appropriate for measuring the adsorption of Rf.[1,2]

In order to optimize an appropriate experimental condition for Rf, in the present study, the equilibration time and distribution ratios for extraction have been measured by batch method experiments with carrier-free radiotracers of Zr and Hf on TTA-resin in the $1.0 \times 10^{-4} - 1.0 \times 10^{-3}$ M HF/1.0×10^{-2} M HNO$_3$ solutions. An online experiment has been also performed for investigating the reversed-phase chromatographic behaviors of Zr and Hf on the TTA resin with Automated Rapid Chemistry Apparatus (ARCA)[3] to simulate the Rf experiments.

The radioisotopes of ^{88}Zr ($t_{1/2} = 83.4$ d) and ^{175}Hf ($t_{1/2} = 70.0$ d) used in the batch experiments were produced by the ^{89}Y($p, 2n$) and ^{175}Lu(p, n) reactions, respectively, at the RIKEN K70 AVF Cyclotron. The short-lived ^{85}Zr and ^{169}Hf isotopes were also produced by the ^{18}O-induced reaction with the ^{nat}Ge and ^{nat}Gd targets, respectively, for the on-line experiments. The TTA-resin was simultaneously produced by mixing the CHP20/P20 resin with a TTA-octanol solution of 50 or 30 wt.%, which includes 50 or 20 wt.% of TTA in n-octanol, respectively. The prepared TTA-resin was used for the batch experiments, as well as for the on-line reversed-phase extraction chromatography. The details of the procedures can be found elsewhere.[2]

In the batch experiments, the D value of 50 wt.% resin was found to be higher than that of the other resin, while the time for chemical equilibration of the former is almost the same as that of the other. The elution curves of Zr and Hf at a flow rate of 0.15 mL/min in the range $1.0 \times 10^{-4} - 1.0 \times 10^{-3}$ M of HF concentration on the former resin are shown in Fig. 1; the peaks of the curves are clearly visible in the figure for all the conditions of HF concentration.

The D values for the on-line experiments are evaluated from the elution curves by using the following equation, $D = V_p/m$ [mL/g], where V_p is the peak volume of an elution curve, and m is the resin weight in a microcolumn. The D values of Zr tend to be higher than those of Hf in the on-line experiments, although, based on the batch experiments, the D value of Hf should be higher than that of Zr at the chemical equilibrium. For instance, in Fig.1(a) the D value of Zr was found to be higher than that of Hf by a factor of 1.2, although in the batch experiments the D value of Zr was found lower than that of Hf by a factor of 2.8. These results in the on-line experiments show that the chemical equilibrium time of Zr is shorter than that of Hf, which agrees with the results of the present batch experiments measured as a function of shaking time. The kinetic behavior observed here should be clarified in order to perform the Rf experiment in the expected project.
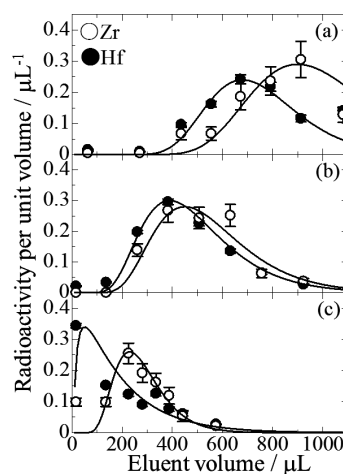

Fig. 1. Elution curves of Zr and Hf against the HF concentration, (a) 1.0×10^{-4} M, (b) 6.0×10^{-4} M, (c) 1.0×10^{-3} M, in the HF/0.010-M HNO$_3$ solution, at a flow rate of 0.15 mL/min. The radioactivity values in the figure represent the values relative to the total eluted radioactivity. Solid lines are curves fitted to a theoretical equation derived by Glückauf model[4].

References

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