## Batch solid-liquid extraction of Nb and Ta with 52 wt% Aliquat 336 resin from HF solutions

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The elements with atomic number  $\geq 104$  are called super-heavy elements. Aqueous-chemistry experiments with these elements have been performed often by using the Automated Rapid Chemical Apparatus (ARCA).<sup>1), 2)</sup> In particular, an anion-exchange experiment of element 105, Db was successfully performed in 13.9 M hydrofluoric acid solution.<sup>2)</sup> However, the chemical species of Db in HF solution were still not clear. Therefore, we studied the liquid-liquid extraction behavior of Nb and Ta, which are lighter homologues of Db, with Aliquat 336 for investigating the charge of complexes of these elements extracted from HF solution.<sup>3)</sup> The results showed that univalent anionic complexes such as  $NbOF_4$  and  $TaF_6$  were extracted. Applying this extraction system to the solid-liquid extraction with Aliquat 336 resin, on-line column chromatography experiments of Nb and Ta with 32 wt% Aliquat 336 resin from HF solutions were conducted using ARCA.<sup>4)</sup> In these experiments, the distribution coefficients ( $K_d$ ) of Nb and Ta in 1-27 M HF solution were calculated from elution peak volume  $(V_p)$  and were compared with the results of a batch experiment. The results showed that the  $K_d$  values of Nb in 5.4 M HF and 10 M HF with ARCA were lower than those obtained from the batch experiment. This probably suggests that the  $K_d$  values of Nb in these HF concentrations were too low because the volume of the resin in micro-columns of ARCA is very small. Therefore, it is necessary to increase the  $K_d$  values of Nb by increasing the amount of Aliquat 336 in the resin. In this work, the batch solid-liquid extraction of Nb and Ta with 52 wt% Aliquat 336 resin was performed.

Long-lived radiotracers,  ${}^{95g}$ Nb ( $T_{1/2} = 34.97$  d) and  ${}^{179}$ Ta ( $T_{1/2} = 665$  d), were produced by deuteron irradiation on Zr and Hf metallic foil targets with natural isotopic abundance, respectively, using the RIKEN K70 AVF Cyclotron. These radiotracers in the targets were chemically isolated by ion exchange. A 52 wt% Aliquat 336 resin was prepared by mixing MCI GEL CHP20/P30 with Aliquat 336 dissolved in methanol for about 1 day, which was followed by drying in an oven at 80 °C.<sup>5)</sup> The  ${}^{95g}$ Nb and  ${}^{179}$ Ta tracers were dissolved in 400 µL of 1-27 M HF and then mixed with 10-15 mg of the 52 wt% Aliquat 336 resin in a syringeless filter tube. After shaking for 5 min, the solution was separated from the resin by filtration, and 250 µL of the solution in each sample was pipetted into another sample tube. For measurement of initial radioactivity,  $A_{ini}$ , in the

aqueous solutions, control experiments without the Aliquat 336 resin were also conducted. The radioactivities of these samples were measured with a Ge detector. The  $K_d$  of <sup>95g</sup>Nb and <sup>179</sup>Ta were obtained using the following equation:

$$K_{\rm d} = \frac{(A_{\rm ini} - A_{\rm s})/m_{\rm r}}{A_{\rm s}/V_{\rm s}}.$$
 (1)

Here,  $A_s$  is the radioactivity of the solution,  $m_r$  is the weight of the resin used and  $V_s$  is the volume of a liquid phase.

The dependences of  $K_d$  values of  ${}^{95g}Nb$  and  ${}^{179}Ta$  on the initial HF concentration, [HF]<sub>ini</sub> were investigated with the 52 wt% Aliquat 336 resin from 1-27 M HF solutions. The obtained results are shown in Fig. 1. In addition, the previous results with 32 wt% Aliquat 336 resin are also shown in Fig. 1.The  $K_d$  values of <sup>179</sup>Ta decreased with increasing [HF]<sub>ini</sub>, while those of <sup>95g</sup>Nb show a minimum at 10 M HF. The obtained behaviors of both elements were similar to those with 32 wt% Aliquat 336 resin, and therefore, the extraction species of those elements are the same for both resins. The lowest  $K_d$  value obtained in this study was about 34 at 10 M HF for Nb. In the previous experiment, the  $K_d$  values obtained from the elution curves in an on-line column experiment were in good agreement with those obtained in a batch experiment in the  $K_{d}$  value range of 30-80. Therefore, it is expected that consistent results between on-line column and batch experiments would be obtained with 52 wt% Aliquat 336 resin. Recently, an on-line column experiment of Nb and Ta with 52 wt% Aliquat 336 resin was performed using ARCA.<sup>6)</sup>



Fig. 1. Adsorption behavior of <sup>95g</sup>Nb and <sup>179</sup>Ta on 32 wt% and 52 wt% Aliquat 336 resin as a function of [HF]<sub>ini</sub>.

## References

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