Extraction behavior of Mo and W from sulfuric acid into Aliquat336 as model experiments for seaborgium (Sg)

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It is known that for inorganic metal complexes such as a sulfato, the ionic radius of the metal center plays an important role in its complex formation. Unlike its lighter homologs, Mo and W the sulfato complex of seaborgium is hard to form, because the theoretically predicted ionic radius of Sg is larger than those of the homologs. Experimental assessment of the sulfato complex formation of Sg, therefore, provides information on its ionic radius, which would be influenced by strong relativistic effects.¹⁾ A rapid solvent extraction apparatus is, however, required to be developed to explore the complex formation of Sg because the half-lives $(T_{1/2})$ of the ^{265a,b}Sg isotopes are so short (around 10 s) and their production cross sections in the 248 Cm(22 Ne, 5n) 265a,b Sg reaction are extremely small.²⁾ In the present study, we examined the extraction behavior of carrier-free ¹⁸¹W ($T_{1/2} = 121.8$ d) using a newly developed Flow Solvent Extractor (FSE) to find suitable experimental conditions for future Sg experiments. On-line experiments with the short-lived ${}^{93m}Mo(T_{1/2} = 6.85 \text{ h})$ and ${}^{179}W(T_{1/2} =$ 37 min) nuclides were also carried out using the FSE connected to a Membrane Degasser (MDG), which was developed for the dissolution of gas-jet transported products.3)

At the RIKEN AVF cyclotron, 93m Mo and 179 W were produced in the nat Nb(d, 2n) 93m Mo and nat Ta(d, xn) 179 W reactions, respectively. The reaction products were transported to the chemistry laboratory by a gas-jet method and were dissolved with 6 M sulfuric acid using the MDG. This aqueous solution was then immediately mixed with an organic solvent of 0.2 M Aliquat336 dissolved in toluene using a spiral PTFE tube with 1-mm inner diameter. The mixture with a volume of 1.5 mL throughout the PTFE tube was collected in a sample vial. After centrifuging, the aqueous and organic solutions were separately taken in measurement tubes for y-ray spectrometry with a Ge detector. The distribution ratio (D) is defined as the ratio of ratio activity per volume between each phase as $D = (A_{org})$ $/V_{org})/(A_{aq}/V_{aq})$, where A_{org} and A_{aq} are radioactivities in the organic and aqueous phases, respectively, and V_{org} and $V_{\rm aq}$ are the volume of the organic and aqueous phases, respectively. Off-line experiments with the relatively long-lived ¹⁸¹W produced in the ^{nat}Ta(d, n)¹⁸¹W reaction were also carried out to compare with the on-line experiments.

In Fig. 1, the variation of the distribution ratios of Mo and W are shown as a function of extraction time, which is the time required to pass through the spiral PTFE tube. In the previous batch-wise extraction experiments, the D values of Mo and W at the equilibrium are approximately 15 and $2^{(4)}$ It is found that, in the off-line experiment, the extraction of ¹⁸¹W reaches the equilibrium in less than 50 s because its Dvalue increases up to the equilibrated value of 2 within 50 s. This equilibration time is much shorter than the time of about 120 s for W observed in our previous experiments.⁴⁾ This result indicates that the extraction kinetics of W was enhanced with the FSE. However, in the on-line experiment, the equilibration time of Mo of approximately 50 s was much longer than that of less than 5 s, $^{4)}$ and the extraction of W did not reach equilibrium within 50 s. This is probably due to slow chemical reactions other than extraction in the MDG and FSE. In future, the kinetics of these elements will be improved by using heating or supersonic systems.



Fig. 1. Dependence of the distribution ratio (D) of Mo and W on extraction time in the spiral PTFE tube of the FSE system.

References

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