Title	Solid-Liquid Extraction of Element 104, Rutherfordium, in Aliquat 336/HCl System : Observation of Equilibration of Chemical Reaction for Transactinide Elements
Author(s)	横北, 卓也
Citation	大阪大学, 2015, 博士論文
Version Type	VoR
URL	https://doi.org/10.18910/52267
rights	
Note	

Solid-Liquid Extraction of Element 104, Rutherfordium, in Aliquat 336/HCl System:
Observation of Equilibration of Chemical Reaction for Transactinide Elements

104番元素ラザホージウムのAliquat 336/HCl系での固液抽出:
超アクチノイド元素の化学平衡到達の観測

By Takuya Yokokita

Graduate School of Science, Osaka University

February, 2015

Abstract

The solid-liquid extraction experiments of the group 4 elements (Zr and Hf), which are homologues of $_{104}$Rf, and a pseudo homologue (Th) by Aliquat 336 from aqueous HCl solutions were performed by a batch method to examine experimental condition and obtain comparison data for the Rf. Distribution coefficients (K_d) were determined as a function of shaking time, indicating that the chemical reactions in the extraction process reach equilibrium with 10 s of shaking. These results suggest that this extraction system is suitable for the Rf ($T_{1/2}$ = 68 s) experiment. The K_d values of these elements in equilibrium were investigated in various HCl concentrations. The results implied that Zr and Hf form anionic chloride complexes, while Th does not form anionic species in all the HCl concentrations studied. In the same purpose, the cation-exchange adsorption and solid-liquid extraction of the group 5 elements (Nb and Ta), which are homologues of the $_{105}$Db, and a pseudo homologue (Pa) by Aliquat 336 resin were also performed by batch method employing HCl. It was found that the chemical reactions for these elements reached equilibrium within 10-s shaking except for Ta. Different distribution behaviors at equilibrium were observed among Nb, Ta, and Pa in cation-exchange adsorption and extraction by Aliquat 336.

A batch-type solid-liquid extraction apparatus was newly designed and constructed to evaluate the time dependency of the distribution behavior of Rf and Db. Using this apparatus, the solid-liquid extraction for Zr and Hf was performed by using the short lived Zr and Hf nuclides produced by nuclear reactions and transported continuously from the nuclear reaction chamber by the He/KCl gas-jet system. The extraction reaction reached equilibrium within 10-s shaking under the present condition. The K_d values of Zr and Hf in the on-line experiment were agreement with those in the off-line experiment except for Hf in 8.2 M HCl.

By using the extraction apparatus, solid-liquid extraction of Rf in the extraction with Aliquat 336 resin from HCl was performed. The equilibration of the extraction reaction of Rf was observed for the first time, and the equilibrated data of Rf were obtained. The K_d values of Rf were increased with an increase in HCl concentration, indicating that Rf formed anionic chloride complexes. The K_d value

of Rf in 9 M HCl was clearly higher than that of Zr and Hf.

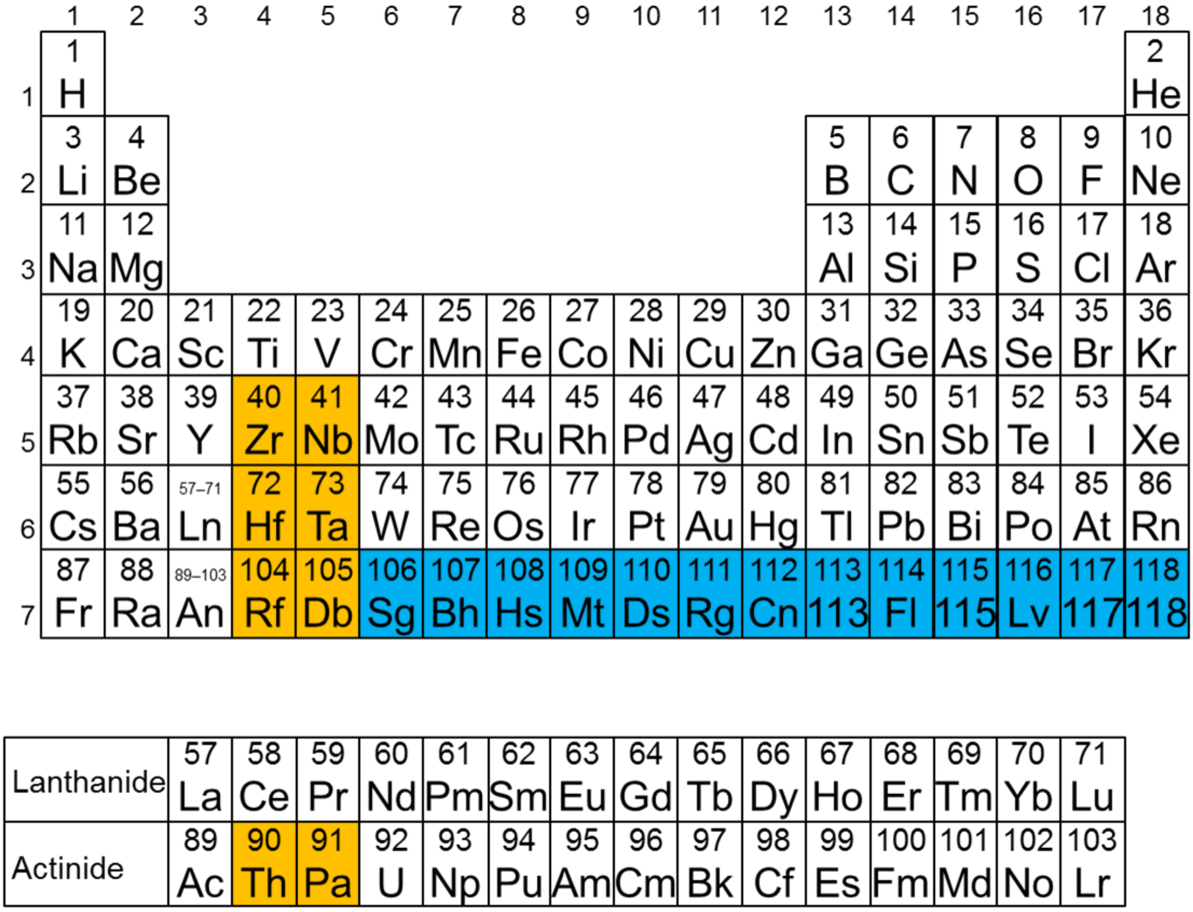
This work will open the systematic study on the complex formation of transactinide elements with various ligands, which would lead to the elucidation of their characteristic chemical properties caused by strong relativistic effect.

Table of Contents

Chapter 1. General Introduction

1.1 Introduction

D. I. Mendeleev proposed the Periodic Table in 1869. Recently, production of element 117 was reported,[1] and the Periodic Table currently contains 118 elements. A current Periodic Table of the elements is shown in Figure 1-1. The Actinide series contains elements of atomic numbers 89 to 103, which fill the 5*f* electron shell. The elements from atomic number 104 to 112 have been predicted to be 6*d* transition metals, and the elements 113–118 to belong to 13–18 group elements. Elements with atomic number $Z \geq 104$ are called transactinide elements (superheavy elements). The chemical properties of transactinide elements are expected to deviate from the periodicity of their lighter homologues in the Periodic Table owning to the strong relativistic effects on valence electronic shells of these heavy atoms.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57–71 Ln	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89–103 An	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 113	114 Fl	115 115	116 Lv	117 117	118 118

Lanthanide	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 1-1. Current Periodic Table. Transactinide elements (superheavy elements) are $Z \geq 104$. Research targets are group 4 elements (Zr, Hf, and Rf), its pseudo homologue (Th), group 5 elements (Nb, Ta, and Db), and its pseudo homologue (Pa).

1.2 Relativistic Effects

The relativistic mass increase is described by

$$m = \frac{m_0}{\sqrt{1-(v/c)^2}}, \tag{1-1}$$

where m_0 is the rest mass of electron, v is the speed of the electron, and c is the speed of light. The Bohr radius (a_B) is given by the following equation.

$$a_\mathrm{B} = \frac{\hbar^2}{mc^2} = a_\mathrm{B}{}^0\sqrt{1-(v/c)^2}. \tag{1-2}$$

Relativistic mass of shell electrons increases due to its velocity approaching to the speed of light enforces the contraction and stabilization of the inner s and $p_{1/2}$ orbital electrons. The increased screening by these contracted orbitals for positive nuclear charge causes the expansion and destabilization of the outer $p_{3/2}$, d, and f orbitals. Relativistic contribution also originates the spin-orbit splitting of levels with orbital angular momenta > 0. The influence of relativistic effects on electron orbital of heavy elements including transactinide elements is significant.[2–4] As an example, energy of atomic orbitals and maximum of the radial charge density of the group 12 elements[4,5] are shown in Figure 1-2(a) and (b), respectively. For element 112, copernicium (Cn), it was predicted that $6d_{3/2}$ and $6d_{5/2}$ orbitals are destabilized and the $7s_{1/2}$ orbital is stabilized by the relativistic effect. The radial charge density of $7s_{1/2}$ orbital would contract and $6d_{5/2}$ orbital expand. The Cn would have the closed-shell electronic ground state configuration Rn: $5f^{14}6d^{10}7s^2$. In element 114, flerovium (Fl), the very large spin-orbit splitting in $7p$ orbital and the strong relativistic stabilization of the $7p_{1/2}$ orbital are expected to result in a quasi-closed-shell configuration Rn: $5f^{14}6d^{10}7s^2 7p_{1/2}{}^2$. It is expected that both Cn and Fl may be more inert than their lighter homologues.[6] Thus, it is important and interesting to study chemical properties of transactinides.

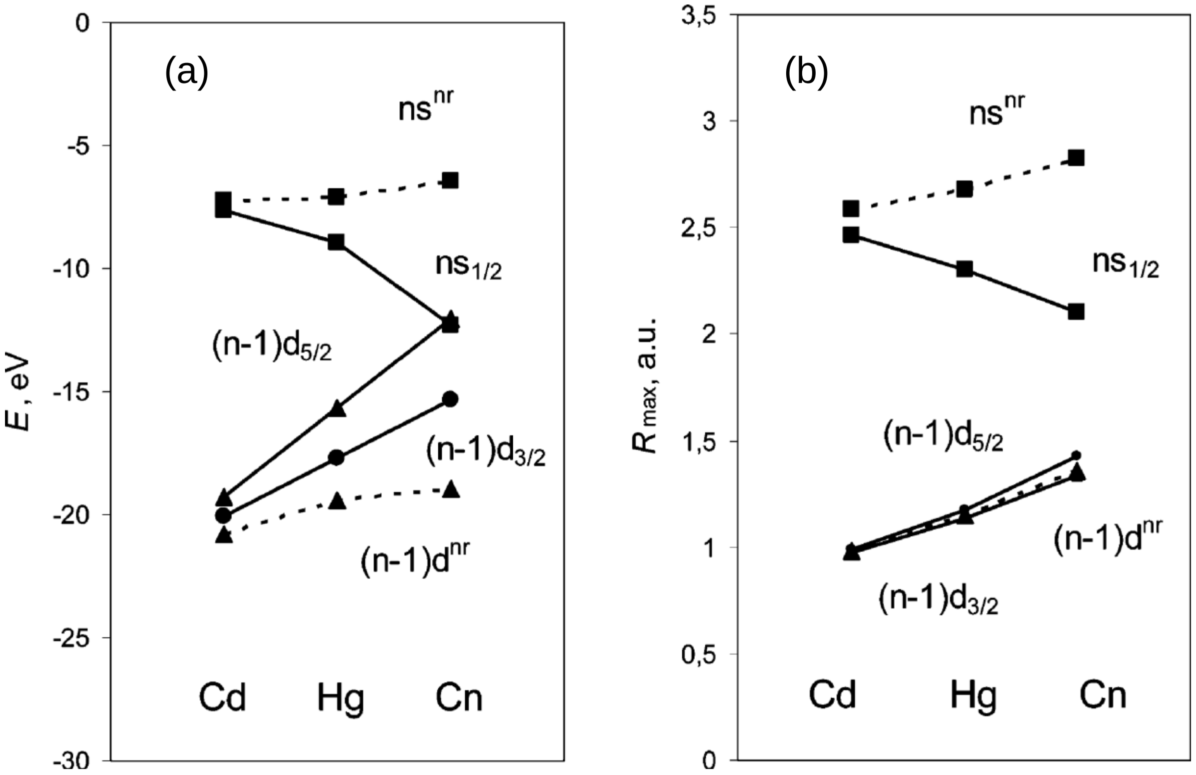


Figure 1-2. (a) Relativistic (solid lines) and nonrelativistic (dashed lines) energies (*E*) of atomic orbitals and (b) the maximum of the radial charge density (R_{max}) of the valence *ns* and (*n*−1)*d* atomic orbitals of group 12 elements, take from references 4 and 5.

1.3 Transactinide Chemistry

One of the most important and interesting questions is the position of transactinide elements in the Periodic Table. Element 92, Uranium (U) is the heaviest naturally-occurring element and all elements of transuranium ($Z \geq 94$) are manmade elements. Nuclei with the atomic number up to 100, fermium (Fm, Z =100), can be produced by stepwise neutron capture in a nuclear reactor, and heavier nuclei including transactinides are produced only in accelerators by heavy-ion-induced nuclear reactions.[2–4]

1.3.1 Production of Transactinide

The transactinide nuclei are mainly produced by two types of the nuclear reactions: cold fusion and hot fusion reactions. Cold-fusion reaction is characterized by relatively low nuclear excitation energies. In the reaction, massive projectile such as ^{50,58}Fe, ^{62,64}Ni, and ^{68,70}Zn fuse with stable targets, ^{208}Pb or ^{209}Bi, and a few neutrons are evaporated. The products in the cold fusion reaction is relatively neutron-deficient nuclei having short half-lives, e.g. ^{257}Rf ($T_{1/2}$ = 4.7 s) produced in the ^{208}Pb(^{50}Ti,n)^{257}Rf reaction. On the other hand, hot-fusion reaction is characterized by relatively high nuclear excitation energies. Actinide targets such as ^{238}U, ^{242,244}Pu, ^{243}Am, ^{248}Cm, ^{249}Bk, ^{249}Cf, and ^{254}Es fuse with light-ion beams such as ^{18}O, ^{22}Ne, and ^{26}Mg. In the reaction, 4 or 5 neutrons are usually emitted and relatively neutron rich nuclei are produced. e.g. ^{248}Cm(^{18}O,5n)^{261}Rf ($T_{1/2}$ = 68 s) reaction.[2–4] By cold-fusion reaction, synthesis of nuclei with Z up to 113 has been reported.[8,9] Hot-fusion reaction leads to the observation of isotopes with $Z \leq 110$.[4,7] Recently, isotopes with $Z \leq 118$ were produced by warm fusion reaction using doubly magic nucleus ^{48}Ca as a projectile and actinide targets.[3,6] In Figure 1-3, experimental production cross section of heavy nuclei for cold fusion, hot fusion, and warm fusion reactions are shown as a function of atomic number.[4] Nuclear reaction cross sections are measured in barn (b); 1 b = 10^{-24} cm^2. For instance, cross section of ^{248}Cm(^{18}O,5n)^{261}Rf reaction is 13 nb,[10] and the production rate of ^{261}Rf nucleus is estimated to about 2 atoms min^{-1} in the bombardment of 500 μg cm^{-2} of ^{248}Cm with 0.5 μA (particle) of ^{18}O beams. The cross sections decreased with an increase in the atomic number.

In summary, heavy nuclides are produced by heavy-ion induced nuclear reactions with very low production rates (≤ several atoms/min). The half-lives of transactinide nuclei are summarized in Table 1-1. Their half-lives are very short ($T_{1/2} \leq 1$ min). These conditions require rapid chemical experiments on single atom scale, restricting potential experiments. Thus, the chemical experiments of transactinides must be rapidly performed on an atom-at-a-time basis; moreover, available experimental methods are restricted.

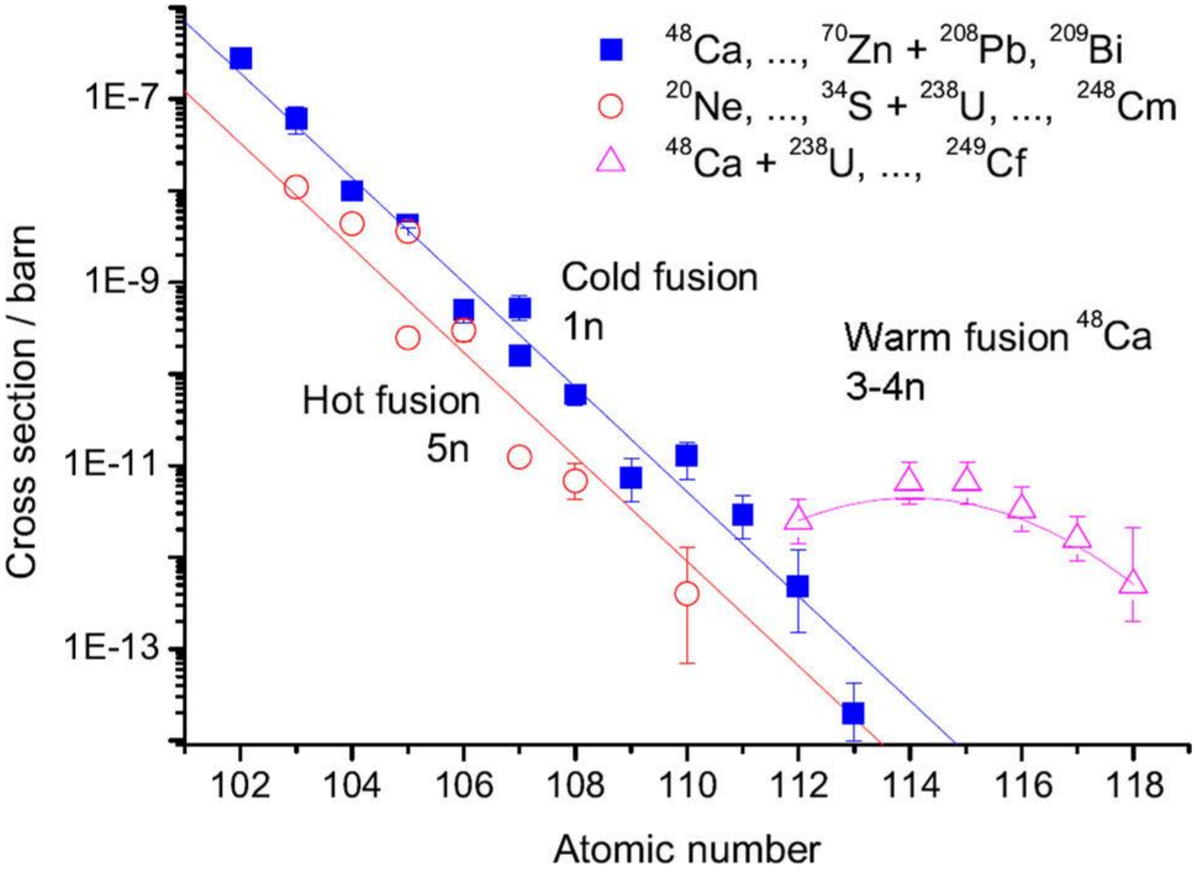


Figure 1-3. Experimental cross sections for the formation of nuclei with heavy nuclei ($Z \geq 102$), take from reference 4. Nuclear reaction cross sections are measured in barn (b); 1 b = 10^{-24} cm^2.

Table 1-1. Half-lives of transactinide nuclei[3]

Atomic number	Mass number	Nuclide	Half-life/s
104	257	^{257}Rf	4.7
104	261	^{261}Rf	68
105	262	^{262}Db	34
105	263	^{263}Db	27
106	265	^{265}Sg	14
107	267	^{267}Bh	17
108	269	^{269}Hs	10
109	276	^{276}Mt	5
110	281	^{281}Ds	26
111	280	^{280}Rg	3.5
112	283	^{283}Cn	3.8
113	285		5.5
114	289	^{289}Fl	2.1
115	289		0.22
116	293		60 m
117	294		~80 m
118	294		0.9 m

1.3.2 Atom-at-a-Time Chemistry

For a chemical reaction

$$bB + xX \leftrightarrows cC + yY. \tag{1-3}$$

the Gibbs energy of the reaction is described with

$$\Delta G = \Delta G^{\circ} + RT\ln\frac{a^{c}(\mathrm{C})a^{y}(\mathrm{Y})}{a^{b}(\mathrm{B})a^{x}(\mathrm{X})}, \tag{1-4}$$

where *a* is the activity. According to the law of mass action, a thermodynamic equilibrium constant, *K*, is represented by

$$\frac{a^{c}(\mathrm{C})a^{y}(\mathrm{Y})}{a^{b}(\mathrm{B})a^{x}(\mathrm{X})} = K. \tag{1-5}$$

at the equilibrium,

$$\Delta G = 0, \tag{1-6}$$

and

$$\Delta G^{\circ} = -RT\ln K. \tag{1-7}$$

These equations are well established for macroscopic quantities of a metal ion M (metal ions M are constituent of B and C at the same time). If a single atom of M is present, it cannot be a constituent of B and C at the same time. At least one of the activity on the B or C cannot exist. For atom-at-a-time chemistry, therefore, the classical low of mass action cannot be held. The concept of chemical equilibrium for single atom is needed. An expression equivalent to the law of mass action was derived by Guillaumont *et al.* in which activities are replaced by a finding probability of the species in the appropriate phase in two-phase distribution. According to this law, the distribution ratio of M between two phases is correctly defined in terms of the finding probabilities of M in one phase or the other phase. If a distribution method is used, this ratio is measured in repetitive experiments. When dynamical distribution methods such as chromatography can be considered as spatially repetitive static partitions, the displacement of M along the chromatographic column, in itself, is a statistical result and only one experiment is necessary. This underlines the validity of distribution experiments with single atoms and the particular attractively of chromatographic methods in atom-at-a-time chemistry.[11] Therefore, transactinide experiments were conducted by distribution method such as chromatography and repetitive experiments with several hundreds or several thousands. Thus, apparatus for rapid and repetitive chemistry is essential.

Typical spectroscopic techniques cannot be applied to the chemical analysis and detection of these elements, and determination of chemical species is difficult. Thus, the chemical properties of transactinides have been so far investigated mainly by a distribution method based on the comparison of their chemical behavior with those of lighter homologous elements (known chemical species, etc.). The chemical properties of transactinides have been so far investigated based on the comparison of their chemical behavior with mainly those of lighter homologous elements.

1.3.3 Experimental Techniques

A flow scheme of the chemical experiment of transactinides is shown in Figure 1-4. The transactinide nuclei are produced by heavy-ion induced nuclear reactions as mentioned above (Subsection 1.3.1). Involatile reaction products recoiling out of the target are usually attached to KCl aerosols seeded in a He gas. Reaction products attached to KCl and volatile products are transported to the chemistry laboratory within a few seconds by the He jet. Chemical experiments with the transported products are performed by simple distribution method such as column chromatography and liquid-liquid extraction for solution chemistry and isothermal chromatography and thermochromatography for gas-phase chemistry. After the chemical separations, the samples are prepared for α-decay spectroscopy and the nuclides are identified.[2–4] Such concatenation experiment is called "on-line" experiment.

For experiments of transactinide, following experiments are needed. (1) "Off-line" experiment should be performed using homologous elements of transactinide to determine the experimental conditions and to obtain the comparison data. (2) Automated and repetitive chemistry apparatuses should be developed. (3) On-line model experiment using the developed apparatus should be performed using homologous elements of transactinide produced by the accelerator. (4) On-line experiment of transactinide should be performed under the determined conditions.

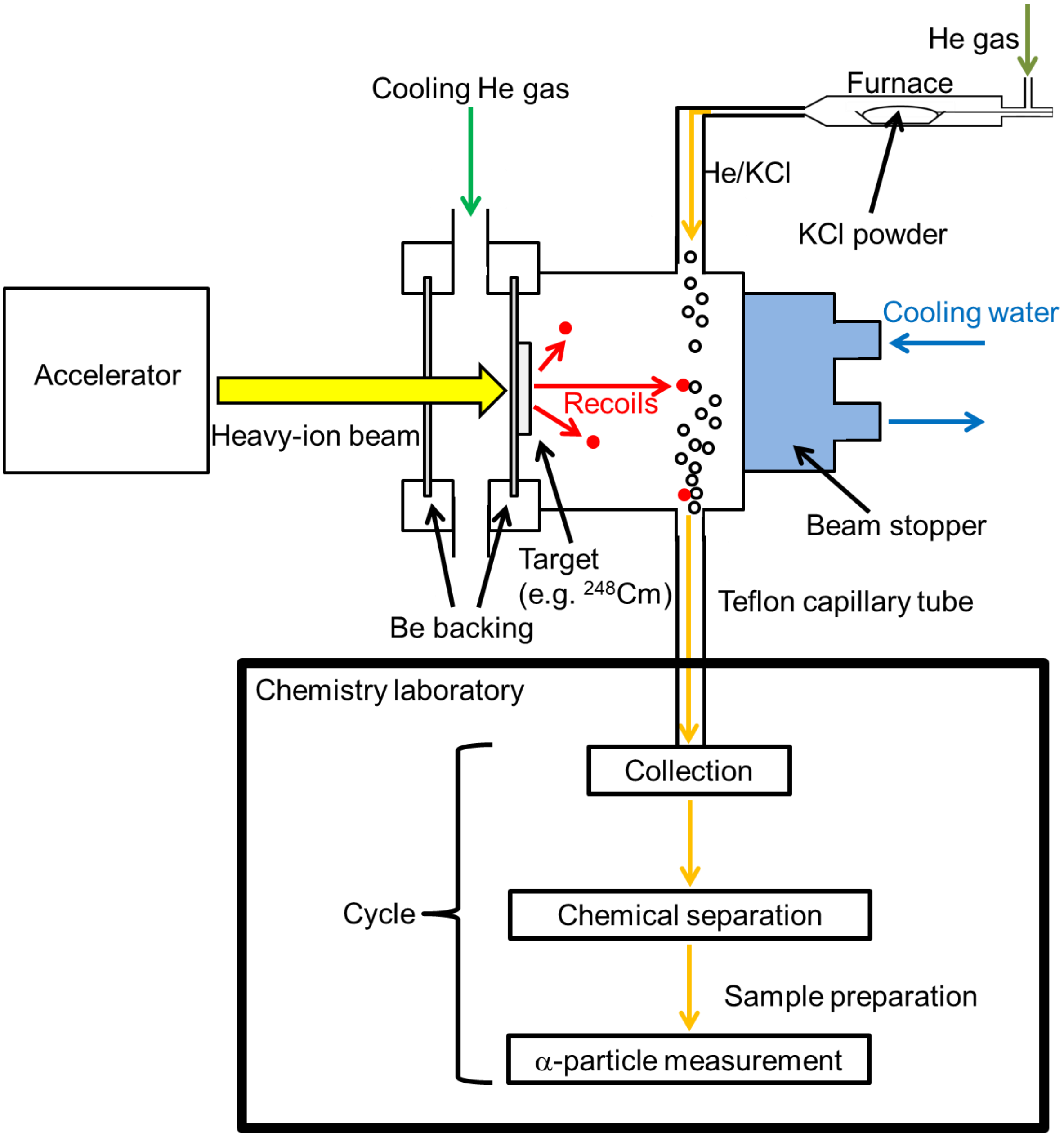


Figure 1-4. Flow scheme for on-line transactinide chemistry experiment.

1.3.4 Previous Chemical Studies on Transactinide Elements

Solution chemistry of transactinides has been carried out for element 104 (rutherfordium, Rf), 105 (dubnium, Db), and 106 (seaborgium, Sg). Gas-phase chemistry of transactinides has been carried out for the elements with the atomic number up to element 108 (hassium, Hs), element 112 (Cn), and element 114 (Fl).

The first pioneering solution chemistry of element 104, Rf, by a cation-exchange chromatography with the ammonium α-hydroxyisobutyrate was conducted by Silva *et al*. in 1970. The Rf species as well as the Zr and Hf species in the group 4 elements were adsorbed on the resin, and this behavior was different from those of the trivalent and divalent actinides. Rf was assigned as a heaviest member of the group 4 family as the next member of the periodic system following the actinide series.[12] Zvára *et al.* performed isothermal and thermochromatography for the Rf chloride. The chromatographic behavior of Rf was similar to that of Hf, and Rf chloride is formed that is much more volatile than actinide chloride.[13] The first solution chemistry of Db was conducted by Gregorich *et al*. with Nb and Ta (group 5 elements), and Db was reported to adsorb on glass surfaces upon fuming with HNO_3.[14] Schädel *et al.* conducted the first Sg, chromatographic experiment. In gas chromatography with $SOCl_2$ and O_2 and cation-exchange chromatography in HNO_3/HF, these chromatographic behaviors of Sg are similar to those of Mo and W in group 6 elements.[15] Eichler *et al.* carried out gas chromatography experiment (reactive gases HCl and O_2) of element 107, bohrium (Bh). A volatile oxychloride compound behavior of Bh was similar to those of group 7 elements (Re and Tc), although Bh showed a lower volatility of its oxychloride compound than Re and Tc.[16] Thermochromatography experiment of tetraoxide of element 108, hassium (Hs) was performed by Düllmann *et al*. The chemical property of Hs is similar to that of the lighter homologue Os. However, adsorption enthalpy of HsO_4 is slightly lower than that of OsO_4.[17] Both Cn and Fl are predicted to be more inert than their homologues by relativistic effect (section 1-2). Therefore, the behaviors of Cn and Fl were compared with those homologues and noble gas. Eichler *et al.* performed thermochromatography of element 112, Cn. Cn was reported to be unlike noble gas Rn, and shows metallic interaction with the gold surface. Cn was found to be considerably more volatile compared to its lighter homologues (Zn, Cd, and Hg), although Cn is a typical element of group 12.[18,19] Yakushev *et al.* carried out combination of isothermal chromactography and themochromatography experiment for Fl. Because observed two atoms of Fl were both adsorbed on gold surface, Fl was concluded to be not inert for a noble gas and still a metal. Fl was reported to be a volatile metal (the least reactive one in group 14 elements).[20] From these studies, transactinide elements with *Z* up to108 have been assigned as *d*-block metal elements belonging to the 7th row of the Periodic Table. Elements 112 and 114 have been shown to be members of group 12 and 14 elements, respectively. As mentioned above, chemical properties of transactinides are similar to those of homologs, though properties of transactinides are slightly different from those of homologs.

Solution chemistry was conducted mainly for element 104, Rf, and element 105, Db. Primary experiments of transactinide elements were carried out by manual method. Recently, these experiments were performed with automated solution chemistry apparatuses: Automated Rapid Chemistry Apparatus (ARCA)[21] for chromatography and Short-lived Isotopes Studied by the AKUFVE technique (SISAK)[23] for liquid-liquid extraction and α-particle measurement (liquid scintillation detector).

1.3.4.1 Previous Studies on Solution Chemistry of Element 104, Rf

First, the mutual separation experiments of Rf were performed to investigated position of Rf in the Periodic Table. By Silva *et al.*, the pioneering work of the cation-exchange experiment of Rf with ammonium alpha hydroxyisobutyrate solution (0.1 M, pH 4.0) was conducted. They demonstrated that the adsorption behavior of Rf on the resin was entirely different from those of trivalent (Cm and Cf) and divalent (No) actinides though similar to those of Zr and Hf.[20] Hulet *et al.* carried out extraction chromatography with trioctylmethylammonium chloride (Aliquat 336) resin from 12 and 6 M HCl. Rf formed anionic complexes in 12 M HCl, and the abundant of the anionic species of Rf was decreased in 6 M HCl. The chloride complexation of Rf is much stronger than that of trivalent actinides and is similar to that of Hf.[24] Szeglowski *et al.* showed that Rf as well as Hf formed anionic fluoride complexes in 0.2 M HF by registering ^{253}Fm–^{253}Es (daughter nuclei of ^{261}Rf) in the multi-column chromatography (cation-, anion-, and cation-exchange columns).[25] Czerwinski *et al.* performed the liquid-liquid extraction of Rf from 12 M HCl into triisooctylamine (TIOA) benzene solution. Rf and Zr were extracted in this system, while Th and Eu were not.[26] From these results, the distribution behaviors of Rf were similar to those of Zr and Hf though trivalent actinides, indicating that Rf belongs to the group 4 elements.

Next, extraction yield, etc. of Rf were compared with those of homologous elements to investigated chemical properties of Rf. In the liquid-liquid extraction from HCl and HCl/LiCl solutions into tributylphosphate (TBP) benzene solutions, extraction behavior of Rf was similar to that of Pu rather than those of Zr and Hf.[27] Bilewicz *et al.* conducted sorption experiment of Rf on glass support surfaces coated with cobalt ferrocyanide. Sorption behavior of Rf was weaker than those of Zr and Hf in ≥ 2 M HCl.[28] Kacher *et al.* carried out liquid-liquid extraction of Rf from HBr and HBr/LiBr solutions with TBP in benzene. In 7.75–9.0 M HBr, Rf was not extracted from HBr, while Zr and Hf were extracted. Rf was extracted with the addition of the salting agent LiBr.[29] In the liquid-liquid extraction from HF with 0.25 M TIOA-xylene, the extraction of group 4 elements decreases in the order Ti > Zr ≈ Hf > Rf.[30] Pfrepper *et al.* performed anion-exchange chromatography of Rf in 0.27 M HF/0.2 and 0.1 M HNO_3 by multi-column technique registering ^{253}Es. In the 0.27 M HF/0.2 M HNO_3, distribution coefficient (K_d) of Hf by on-line column chromatography agreed with that by the off-line batch method. It is indicating that the K_d values of Hf in equilibrium in the on-line experiment. From the slope analysis of log K_d versus log [HNO_3] plots, they proposed that Rf formed $[RfF_6]^{2-}$.[31] Schumann *et al.* investigated cation-exchange behavior of Rf in 0.1 M HCl/0.01 M HF. Rf and Th adsorbed on the resin, while Hf did not adsorbed on the resin. From this result, cation-exchange behavior of Rf was similar to that of Th, and the fluoride complex formation was in the order as Zr > Hf » Rf > Th.[32] Bilewicz studied adsorption of Zr^{4+}, Hf^{4+}, Rf^{4+}, and Po^{4+} on thenoyltrifluoroacetone (TTA)-hydrophobized glass surface. Adsorption behavior of Rf was different from those of Zr and Hf.[33]

By using ARCA, systematic studies in various acidic concentrations were performed. Brüchle *et al.* performed reverse-phase chromatography with TBP resin from 8 M HCl using ARCA. The sequence of the K_d values was Zr > Rf > Hf. This result was in agreement with that obtained by Czerwinski, *et al*[27].[34,35] Cation- and anion-exchange chromatographies on Rf in HF/0.1 M HNO_3 using ARCA was performed by Strub *et al*. In this experiment, the K_d values of Hf in on-line chromatography agreed with those in off-line batch experiment. In the cation exchange, the K_d values of Rf decreased with increasing HF concentration from 0.1 M HNO_3/0.03 M to 0.05 M HF. In the HF concentration range, in which K_d values of Rf decrease is one order higher than that of Zr and Hf, the cation-exchange behavior of Rf was similar to that of Th rather than those of Zr and Hf. In the anion exchange, the behavior of Rf was similar to that of Th and not to those of Zr and Hf. This result was not consistent with the previous one obtained by Pfrepper *et al*[31]. In anion exchange in 0.05 M HF, the K_d values of Rf and Hf were increased with a decrease of the HNO_3 concentration.[36] To adjust a discrepancy between report of Pfrepper *et al.*[31] and that of Strub *et al.*[36], Kronenberg *et al.* studied anion-exchange behavior of Rf in 0.5 M HF/0.1 M HNO_3 and 0.01 M HF using multi-column technique registering ^{253}Es. In this experiment, the K_d values of Hf in off-line batch experiment agreed with those in on-line column chromatography experiment. The K_d values for Rf are low in the presence of 0.1 M HNO_3 and drastically increases with decreased NO_3^- (counterion) concentration. From this result and that by Strub *et al.*[36], they reported that the competition of the NO_3^- for the exchanging sites on the anion-exchange resin of anionic Rf fluoride was stronger than that of Zr and Hf fluoride.[37] Even *et al.* performed anion-exchange chromatography using physical preseparator and ARCA. Owing to preseparator, the background was 0.48 events/481 h in alpha energy range of ^{261}Rf and ^{257}No. The percent adsorption of Rf were ≥ 67.1% in 7×10^{-4} M HF and were ≥ 74.5% in 1×10^{-3} M HF.[38]

In SISAK, to use liquid scintillation detector, preseparation technique was used for reducing background. Omtvedt *et al.* studied liquid-liquid extraction of ^{257}Rf from 6 M HNO_3 by 0.25 M dibutyl-phosphoric acid in toluene solution using SISAK. The approximately 50% of Rf was extracted and the extraction behavior of Rf was similar to those of Zr and Hf. They suggested that extraction in the SISAK centrifuges was too fast to achieve equilibrium, thus the data could not be directly compared to the data from batch experiments under equilibrium conditions.[39] The liquid-liquid extraction of Rf from H_2SO_4 with trioctylamine (TOA) in toluene solution using SISAK was also performed. The extraction yield of Rf was lower than those of Zr and Hf, and the result was in good agreement with a theoretical calculation.[23]

Several experiments of Rf were performed by using Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) which is ARCA for chromatographic experiments coupled with the passivated ion-implanted planner silicon (PIPS) detector for α spectroscopy. A schematic diagram of AIDA[10] is shown in Figure 1-5. By using AIDA, the chloride,[40–42] nitrate,[40] fluoride,[43–47] and sulfate[48] complexes of Rf were studied. Anion-exchange chromatography of Rf in HCl was conducted by Haba *et al*., and Figure 1-6 shows variation of the percent adsorption as a function of HCl concentration. In this study, the solution containing Rf was fed onto a column at 80 ºC. Rf formed anionic complexes in 7.0–9.5 M HCl, and percent adsorption sequence was Rf > Zr > Hf in 9.0 M HCl.[40] In a TBP/HCl system, percent extractions of Rf as well as Zr and Hf were increased as the concentration of HCl increased in 7.2–8.0 M HCl. Percent extraction order was found to be Zr > Hf ≈ Rf.[41] Extraction chromatography of Rf in a trioctylphosphine oxide (TOPO)/HCl system was performed by Toyoshima *et al*. The percent extractions of Rf as well as Zr and Hf increased with increasing the HCl concentration in 2.0–7.0 M HCl. The extraction order was Zr

> Hf ≥ Rf, which was a similar trend to that observed in TBP[41].[42] Haba *et al.* carried out the anion-exchange chromatography of Rf in 8.0 M HNO_3. In this condition, Rf forms cationic or neutral species like Zr and Hf but not like Th and Pu.[40] In the anion- and cation-exchange experiments of fluoride complexes, the K_d values of Zr and Hf in the on-line column experiment using AIDA were in good agreement with those in the off-line batch experiment, and the K_d values of Rf were obtained under the same conditions.[43–47] Haba *et al.* studied anion-exchange chromatography of Rf in 1.9–13.9 M HF. The adsorption of Rf on the anion-exchange resin was smaller than that of Zr and Hf. From the slope analysis of log K_d versus log $[HF]_{ini}$, the anionic species of Rf, Zr, and Hf were proposed as $[RfF_6]^{2-}$ for Rf, $[ZrF_7]^{3-}$ for Zr, and $[HfF_7]^{3-}$ for Hf.[43] Toyoshima *et al.* studied elution curve of Rf in anion-exchange chromatography in 5.4 M HF for the first time an atom-at-a-time basis. The obtained K_d value of Rf was smaller than that of Hf and agreed with the K_d value by Haba *et al*[43].[44] In the anion-exchange chromatography in HF/HNO_3, the K_d values of Rf were smaller than those of Zr and Hf, and the K_d values of these elements decreased with an increase of the $[NO_3^-]_{eq}$[31]. Figure 1-7 shows log K_d of Zr, Hf, and Rf versus log $[NO_3^-]_{eq}$, and the slope values of log K_d versus log $[NO_3^-]_{eq}$ of these elements were all about −2 in $[F^-]_{eq} = 3.0 \times 10^{-3}$ M for Rf and in $[F^-]_{eq} = 10^{-5}$–10^{-2} M solutions for Zr and Hf. The $[RfF_6]^{2-}$ was proposed in this fluoride ion concentration.[45] Ishii *et al.* performed the cation-exchange chromatography of Rf in HF/HNO_3. The K_d values of Rf decreased with an increase of the fluoride ion concentrations. The sequence of the K_d values was Zr ≈ Hf > Rf > Th, which was reverse order of ionic radii. This sequence agreed with a theoretical calculation by Pershina *et al*[49]. In $[F^-] = 1.06 \times 10^{-4}$ M solution, slope values of log K_d versus log $[H^+]$ of Rf was -2.2 ± 0.5, suggesting that the Rf species were $[RfF]^{3+}$ and $[RfF_2]^{2+}$ similar to Zr, Hf, and Th.[46,47] From these results, it was not found that the ion-exchange behavior of fluoride complexes of Rf were clearly different from those of Zr, Hf, and Th. Li *et al.* studied the cation-exchange behavior of Rf in 0.15–0.69 M H_2SO_4/HNO_3 ($[H^+]$ = 1.0 M). Figure 1-7 shows dependence of the K_d values of Zr and Hf on the HSO_4^- concentration. At 60 °C, the K_d values of Hf in on-line experiment were in good agreement with those in off-line batch experiment, although the K_d values of Zr in on-line experiment were not. Under these conditions, the K_d values of Rf was obtained. Percent adsorptions of Rf, Zr, and Hf decreased with an

increases of HSO_4^- concentration, indicating the successive formation of sulfate complexes of these elements, and Rf showed a much weaker tendency to form sulfate complexes than Zr and Hf. This experimental result was consistent with theoretical predictions[50]. [48] However, the chemical reactions in the cation exchange of Rf might not reach to equilibrium.

Therefore, the data of fluoride complexes of Rf were obtained in the equilibria for the homologues,[31,36,37,43–47,58,59] and linear correlation between the K_d values and concentration of the counterion were observed.[31,43,45,47] On the other hand, the data of Rf in other inorganic ligand solutions were obtained in the non-equilibria for the homologues, and inconsistent results were reported.

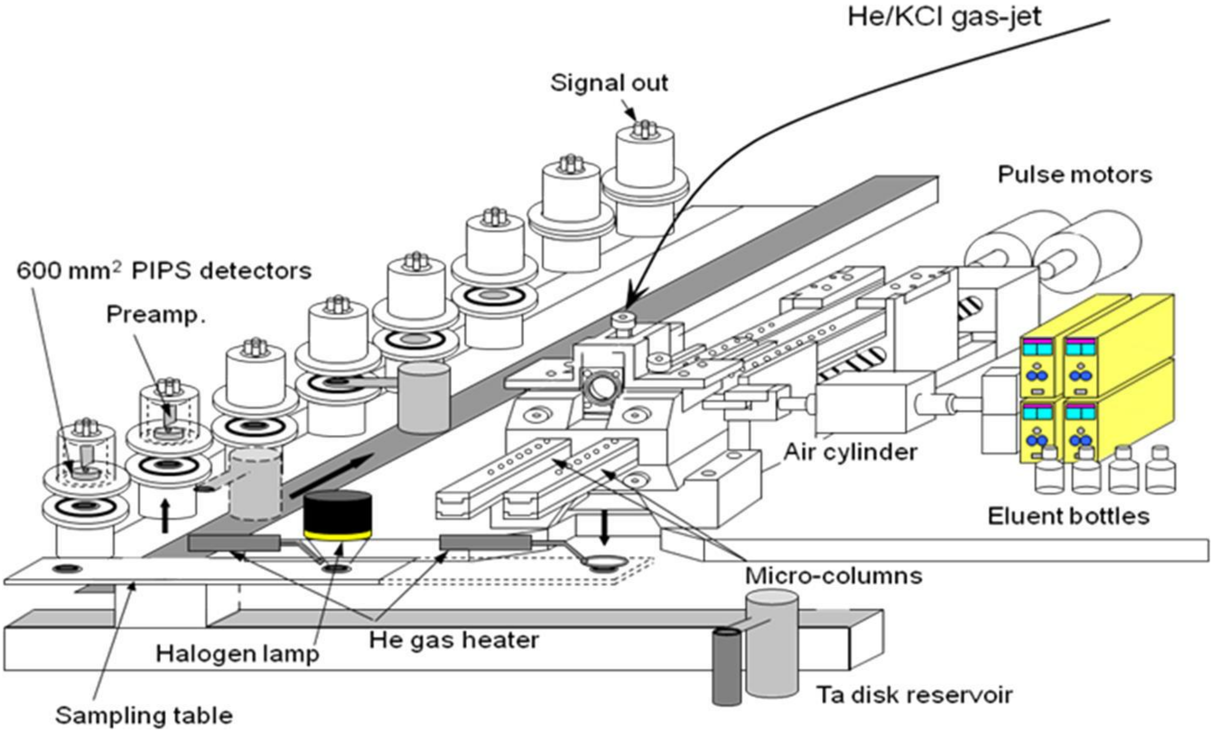


Figure 1-5. Schematic drawing of AIDA, take from reference 10.

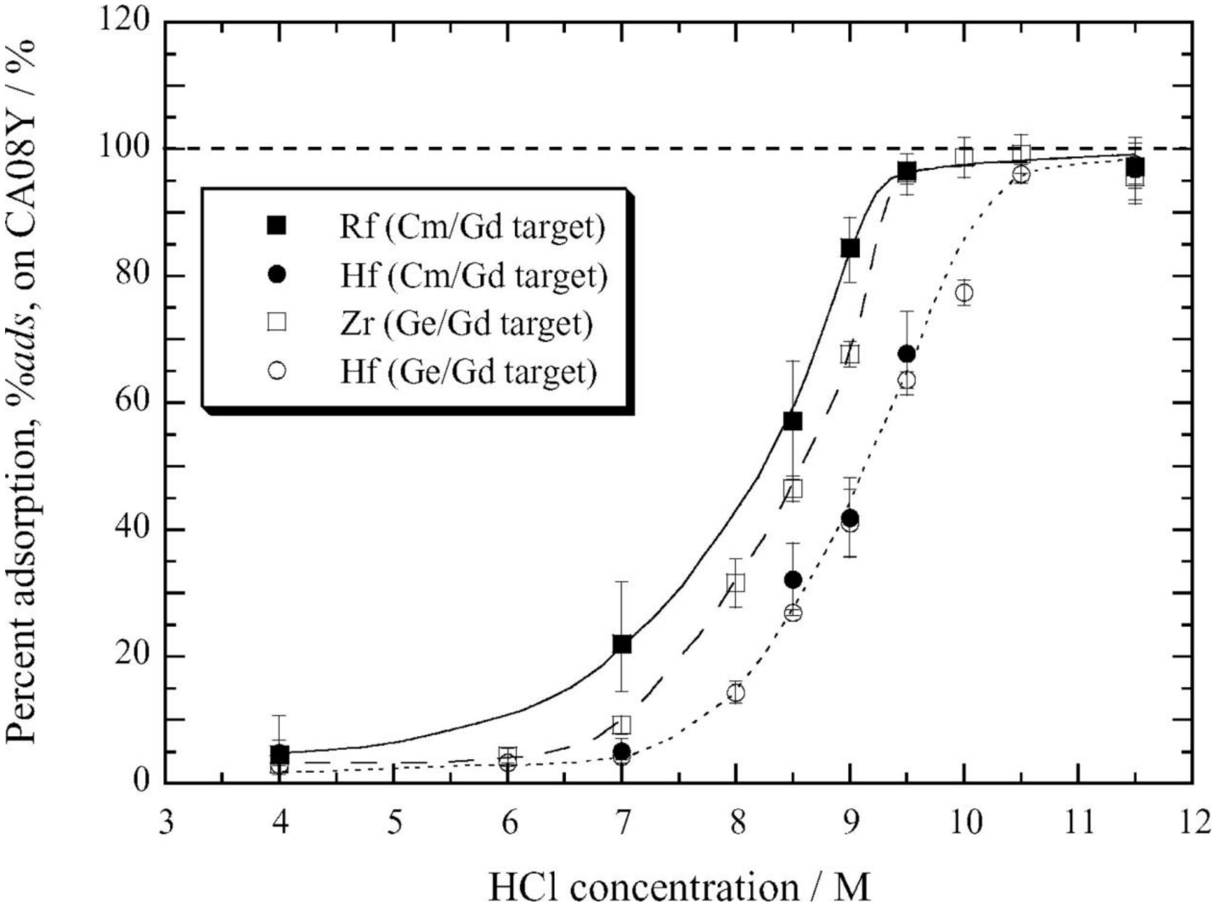


Figure 1-6. The percent adsorption of Rf, Zr, and Hf as a function of the HCl concentration during anion exchange, take from reference 40.

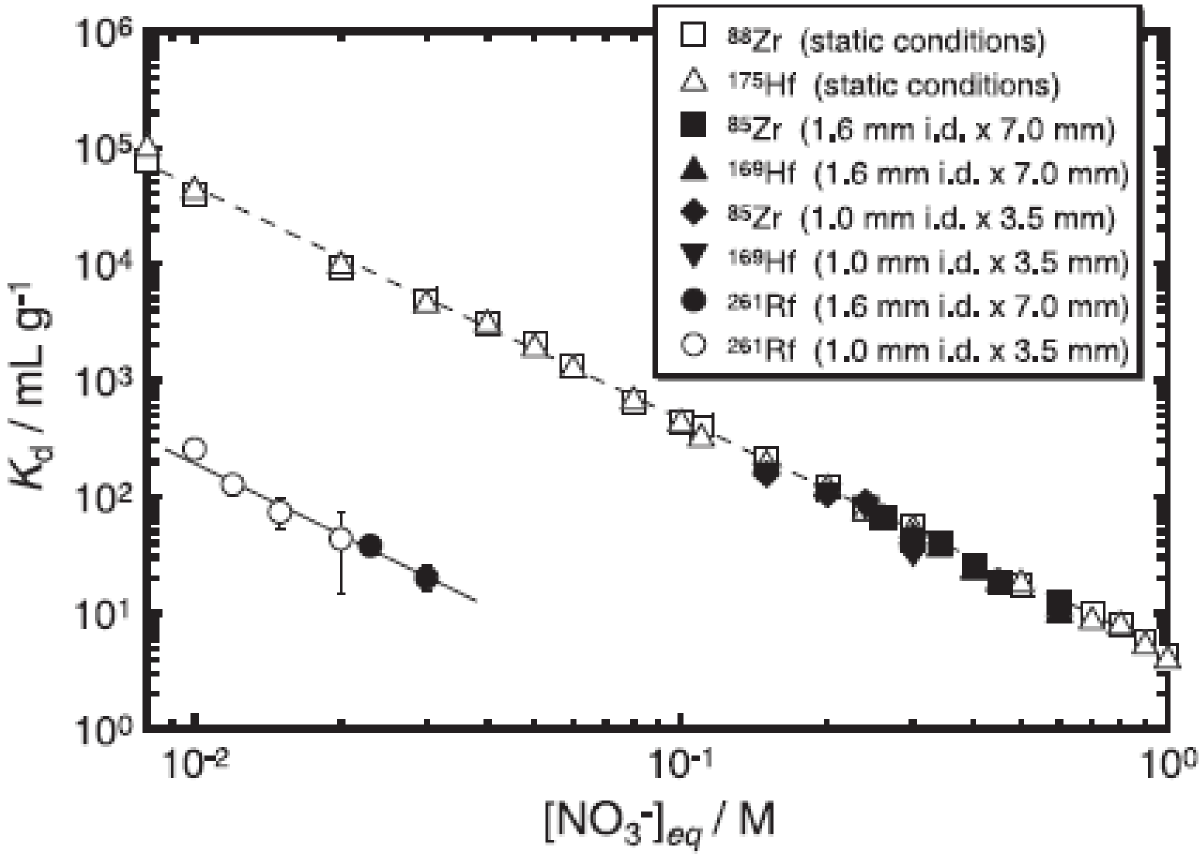


Figure 1-7. The K_d values of Zr, Hf, and Rf as a function of the equilibrated concentration of NO_3^- during anion exchange at the constant equilibrated F^- concentration of 3.0×10^{-3} M, take from reference 45.

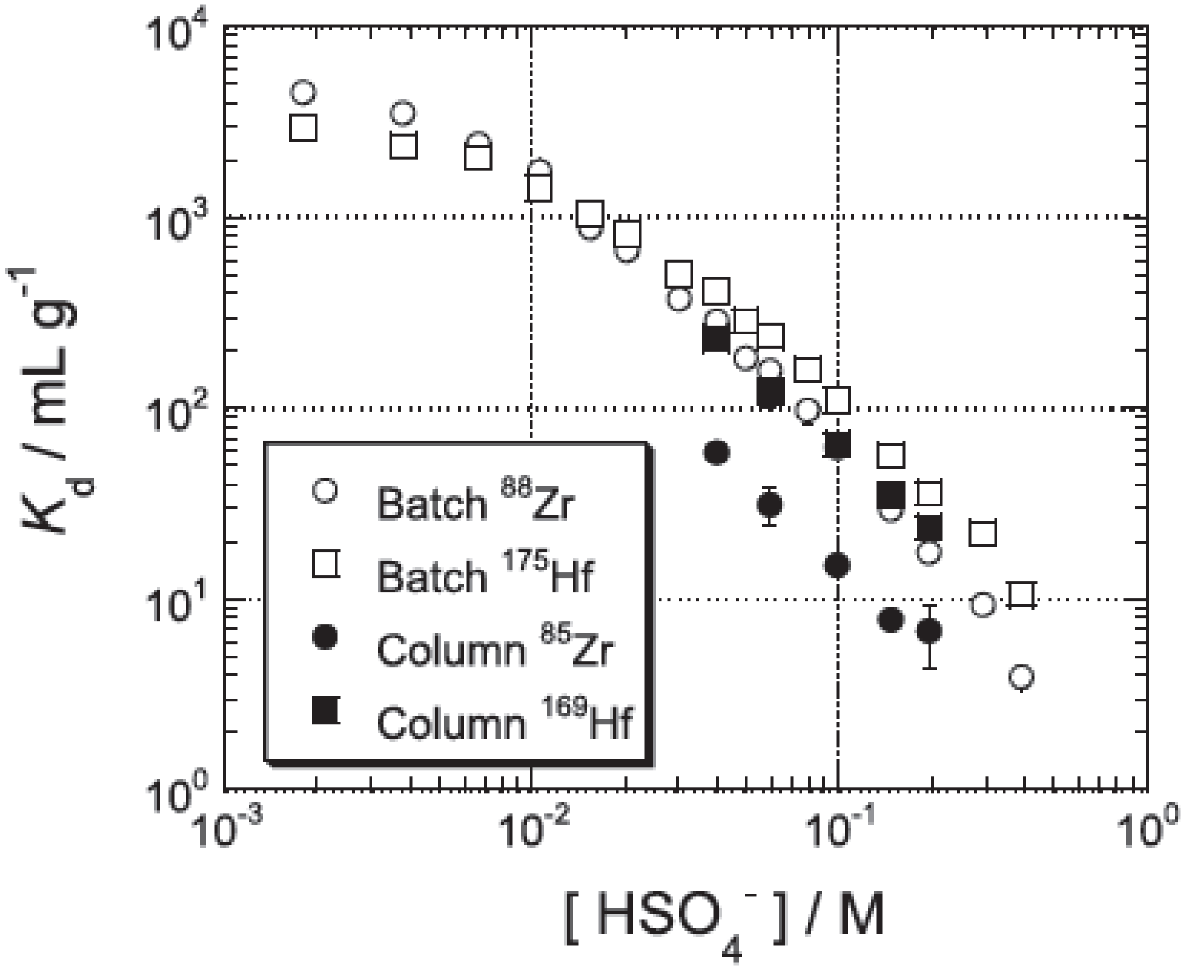


Figure 1-8. The K_d values of Zr and Hf as a function of the HSO_4^- concentration at the constant H+ concentration of 1.0 M during cation exchange, take from reference 48.

1.3.4.2 Previous Studies on Solution Chemistry of Element 105, Db

Gregorich *et al.* performed the first solution chemistry experiment of Db. Db adsorbed on glass surfaces in fuming with 15 M HNO_3. After washing by 1.5 M HNO_3, the Db remain adsorbed onto glass, which was a characteristic property for the group 5 elements. On the other hand, in liquid-liquid extraction, Db as well as Ta was extracted from 3.8 M HNO_3/1.1 M HF with methyl isobutyl ketone (MIBK) in which Nb did not.[14] Kratz *et al.* studied extraction chromatographic behavior of Db with TIOA using ARCA. Db was extracted into TIOA from 12 M HCl/0.02 M HF and 10 M HCl, similarly to Nb, Ta, and Pa, which indicated that Db formed some anionic halide complexes. Db was found in a Nb and Pa fraction (4 M HCl/0.02 M HF) and was not found in a Ta fraction (6 M HNO_3/0.015 M HF), suggesting that the anionic halide complexes of Db were different from those of Ta, and similar to those of Nb and Pa.[51] Zimmermann *et al.* performed additional experiment. In 0.5 M HCl/0.01 M HF, extraction behavior of Db was similar to that of Pa rather than that of Nb and clearly different from that of Ta.[52] Extraction behaviors of Db with diisobutylcarbinol from concentrated HBr, 6 M HCl/0.0002 M HF, and 0.5 M HCl using ARCA was studied by Gober *et al*. From concentrated HBr, the extraction yield of Db was 30–40%, and extraction sequence was Pa > Nb > Db. Because the extraction into diisobutylcarbinol is restricted to neutral or singly charged metal complexes, the tendency of Db to form polynegative complexes was stronger than that of Nb and much stronger than that of Pa at high halide concentration.[53] Cation-exchange chromatography of Db in 0.05 M α-hydroxyisobutyric acid using ARCA was performed by Schädel *et al*. Db was eluted from the column together with the pentavalent Nb, Ta, and Pa ions, while tetravalent Zr ion and trivalent Eu ion were strongly retained on the column.[54] Trubert *et al.* carried out the anion exchange of Db by the multi-column technique registering ^{254}Fm (daughter nuclide of ^{262}Db). In 0.2 M HF, Db was strongly retained on the anion exchanger.[55]

After above fundamental solution chemistry of Db, four experiments determining the K_d values were performed. Paulus *et al.* performed reverse-phase chromatography of Db with Aliquat 336 resin in 6 M HCl and 4 M HF. In this study, the K_d value of Db was for the first time obtained. The K_d

values were in the sequence of Pa > Nb ≥ Db > Ta in an Aliquat 336/6 M HCl system. The lowest limit of K_d value was determined in an Aliquat 336/4 M HF experiment, and extraction behavior of Db was similar to that of Nb and Ta and different from that of Pa.[56,57] In this pioneering work, it is not clear whether the reactions of these metals in HCl reached equilibria even for Nb, Ta, and Pa, because mixing time of two phases was fixed for 2 min. Two experiments of anion-exchange chromatography of fluoride complexes of Db were performed. The K_d values of Db were obtained under the condition that the K_d values of Nb and Ta obtained in the on-line experiment agreed with those in the off-line batch experiment.[58,59] Tsukada *et al.* investigated anion-exchange chromatographic behavior of Db in 13.9 M HCl using AIDA, and the obtained sequence of K_d values was Ta ≈ Nb > Db ≥ Pa.[58] To shorten the time for the sample preparation of α-ray sources, AIDA-II was developed[22]. Kasamatsu *et al.* performed anion-exchange chromatography of Db in 0.31 M HF/0.1 M HNO_3 using AIDA-II, and adsorption behavior of Db was weaker than Ta and similar to Nb and Pa in dilute fluoride ion concentration (0.003 M). From the result, Db would form an oxofluoride complex.[59]

1.4 Aim of This Work

Pioneering chemical studies on transactinides revealed that these elements belong to *d* block element in the 7th row in the Periodic Table from similarity with the chemical behavior of homologous elements. For the study of further detailed chemical properties such as complex formation, the equilibrated data such as K_d are needed. However, equilibration of the chemical reactions has not been confirmed for the transactinide elements. Ion-exchange experiments for the only fluoride complexation of Rf and Db were successfully performed under conditions such that ion-exchange behaviors in equilibria were observed for their homologues.[31,36,37,43–47,58,59] Especially for Rf, the linear correlation between the K_d values and concentration of the counterion were observed,[31,43,45,47] and the ion-exchange behaviors of Rf were clearly different from those of Zr and Hf. The chemical reaction kinetics is possibly different among the homologues. Indeed, that of Zr was reported to be different from that of Hf in cation exchange in H_2SO_4/HNO_3.[48] Therefore, it is important to investigate of time dependence of the distribution behavior of transactinides to investigate chemical properties of transactinides.

Aim of this work is observation of the equilibration of the distribution behavior of Rf and Db in solid-liquid extraction by investigating the time dependence of its distribution behavior. Based on these results, we would obtain the equilibrated K_d values. For this propose, the following experiments are needed. Rapid distribution reaction system which can be applied to short-lived Rf and Db nuclides: ^{261}Rf ($T_{1/2}$ = 68 s) and ^{262}Db ($T_{1/2}$ = 34 s), should be found. To investigate time dependence of the distribution behavior, a new automated and repetitive chemistry apparatus, which is connected with a He/KCl gas-jet transportation system for nuclear reaction products, should be developed. On-line test experiment using the developed apparatus should be performed using radionuclides of homologous elements of Rf: Zr and Hf and Db: Nb and Ta, produced in nuclear reactions. On-line experiment of Rf and Db should be performed under the determined conditions.

The purpose of this work is to study the distribution behaviors of ^{261}Rf and ^{262}Db, production at the K70 AVF (Azimuthally Varying Field) cyclotron at RIKEN, using a solid-liquid extraction apparatus for distribution experiment and Automated rapid α/SF detection system[60] for the identification of the nuclides. In our research group, a solid-liquid extraction apparatus, AutoMated Batch-type solid-liquid Extraction apparatus for Repetitive experiments of transactinides (AMBER), was under development to investigate the time required to reach equilibrium.[61] In this research, following studies were conducted.

(1) Solid-liquid extraction of homologous elements of Rf and Db from HCl

(2) Development of an automated batch-type solid-liquid extraction apparatus and solid-liquid extraction of Zr and Hf with Aliquat 336 from HCl

(3) Solid-liquid extraction of Rf with Aliquat 336 from HCl

(1) Solid-liquid extraction of homologous elements of Rf and Db from HCl (Chapter 2)

In the previous study of our group, we carried out solid-liquid extraction of Zr, Hf, and Th with TIOA resin in HCl.[61] In this chemical reaction system chemical reactions were sufficiently fast to study extraction behavior of Rf. However, the K_d values were decreased with reusing the same TIOA resin. The TIOA resin was able to be repetitively used only about 5 times because the Zr and Hf species adsorbed on the resin were stripped by washing the resin with 0.01 M HF/6 M HNO_3. This is a large problem in transactinide experiments, because typical repetition in transactinide experiment is more than several hundred times.[62] In this study, quaternary ammonium chloride Aliquat 336 (anion extractor) was used for extractant batch extraction and solid-liquid extraction using carrier-free radioisotope (RI) tracers of Zr, Hf, and Th was carried out in an Aliquat 336/HCl system.

The separation of Nb from Ta can be conducted in HCl by extraction with amines using the difference of chloride complex likely to form.[63] For this reason, the chloride complexation of Db is very attractive. Though, inconsistent distribution behaviors were reported among some experiments in anion exchange and extraction by amine extractants for both Nb and Ta.[56,57,64–76] As reasons for this, polymerization,[63] adsorptive property,[14] and non-equilibrium in distribution reactions of these elements are considered. The behavior of Db is need to compared with those of the mononuclear species of Nb, Ta, and Pa, because Db exists as only one atom at a time and has not undergo polymerization. Thus, experiments are needed to carry out using too low metal concentration sample (carrier-free RI tracers) to form polynuclear species. In this study, distribution behavior in equilibria of Nb, Ta, and Pa in cation exchange and extraction by Aliquat 336 from HCl were studied after investigation of adsorption properties of these elements. Based on these results, we conclude with a proposal of suitable experimental conditions for Db.

(2) Development of an automated batch-type solid-liquid extraction apparatus and solid-liquid extraction of Zr and Hf with Aliquat 336 from HCl (Chapter 3)

Chemical reaction container of AMBER exists two problems; leaky and reflux of the solution.[62] To resolve these problems, a new chemical reaction container was developed. Solid-liquid extraction of Zr and Hf was also carried out using AMBER to evaluate repetitive extraction experiment reusing the resin in the off-line experiment. Then, on-line solid-liquid extraction experiment of Zr and Hf was performed in Research Center for Nuclear Physics (RCNP), Osaka University.

(3) Solid-liquid extraction of Rf with Aliquat 336 from HCl (Chapter 4)

To investigate distribution behaviors of Rf and obtain the data in equilibrium, ^{261}Rf ($T_{1/2}$ = 68 s) was produced in the ^{248}Cm(^{18}O,5n)^{261}Rf reaction and carried out solid-liquid extraction experiment in the Aliquat 336/HCl system using AMBER at RIKEN.

Based on these results, comprehensive discussion was performed in Chapter 5.

Chapter 2. Solid-Liquid Extraction of Homologous Elements of Rf and Db from HCl

2.1 Introduction

The solution chemistry of element 104, Rf, was mainly carried out in comparison of its behavior with those of Zr and Hf (group 4 elements), and Th (pseudo homologue). Several experiments on the chloride complexes of Rf were reported[24,26,27,29,34,35,40–42] and three of which were studies of the anionic chloride complexes of Rf.[24,26,40] From these studies, it was reported that Rf as well as Zr and Hf formed anionic chloride complexes. Haba *et al.* reported that the anion-exchange chromatographic behavior of Rf was investigated in a wide range of HCl concentration. In this experiment, Rf was dissolved in concentrated hot HCl (80 ºC) and fed onto a column, and only percent adsorption were obtained (the K_d values were not obtained).[10,40] Although these pioneering Rf experiments[24,26,40] are important to deduce the chemical behavior of anionic chloride complexes of Rf, equilibration of the chemical reactions was not confirmed for either Zr or Hf. Equilibrated data are needed to investigate chemical properties such as complex formation constant. In our previous study, solid-liquid extraction equilibrium in a TIOA/HCl system of Zr and Hf was investigated, and the reactions with the higher than 30 wt% TIOA resins were equilibrated within 10 s.[61] However, the extraction with TIOA has problem for repetitive experiment, because the same resin can only be reused about five times.[62]

In this study, carrier-free RI tracers of ^{88}Zr, ^{175}Hf, and ^{234}Th were produced and purified. First these adsorption behaviors on the surface of the polypropylene (PP) tubes were studied. Subsequently, solid-liquid extraction of Zr(IV), Hf(IV), and Th(IV) with Aliquat 336 resin from HCl by batch method was investigated. The time required to reach equilibrium in the solid-liquid extraction for Zr, Hf, and Th, and examined variation in their K_d values in equilibrium for different HCl concentrations were investigated. Herein, the number of repetitive experiments was not considered (this experiment was Chapter 3), and to find the suitable experimental conditions and to obtain the comparison data for Rf, the solid-liquid extraction experiments were studied.

The solution chemistry of element 105, Db, was carried out in comparison of its behavior with those of Nb and Ta (group 5 elements), and Pa (pseudo homologue). In HF, Nb and Ta exist as monomeric complexes, $[\mathrm{NbOF}_n]^{3-n}$, $[\mathrm{Nb(OH)}_2\mathrm{F}_n]^{3-n}$, $[\mathrm{NbF}_n]^{5-n}$ (in highly concentrated HF), $[\mathrm{TaF}_n]^{5-n}$, and $[\mathrm{TaOF}_n]^{3-n}$ (in dilute HF).[63,83–86] Several solution chemical experiments of Db were conducted in HF or HF/mineral acid mixer solutions, and only two solution chemical experiments of Db in pure HCl were reported. From extraction chromatography of Db with TIOA from 10 M HCl, the Db as well as the Nb, Ta, and Pa forms anionic chloride complexes.[51] In an Aliquat 336/6 M HCl system, the K_d values were in the sequence of Pa > Nb ≥ Db > Ta.[56,57] In these pioneering works,[51,56,57] it was not clear whether the reactions of these metals in HCl reached equilibria even for Nb, Ta, and Pa. Therefore, the distribution data for Db in distribution equilibrium are needed in order to investigate the detailed chloride complex formation of Db. The distribution data for Nb, Ta, and Pa in equilibria should be also obtained for the comparison.

Herein, carrier-free RI tracers of $^{95}\mathrm{Nb}$, $^{177,179}\mathrm{Ta}$, and $^{233}\mathrm{Pa}$ were produced and purified. First these adsorption behaviors of Nb(V), Ta(V), and Pa(V) on the surface of the PP tubes were studied. Subsequently, cation exchange and solid-liquid extraction by Aliquat 336 of these elements were performed on these tracers using HCl. The time required to reach equilibrium in the distribution reaction for Nb, Ta, and Pa, and examined variations in their K_d values in equilibrium for different HCl and Aliquat 336 concentrations were investigated. Based on these results, the suitable experimental conditions for Db experiment were proposed.

2.2 Solid-Liquid Extraction of Zr, Hf, and Th in an Aliquat 336/HCl System

2.2.1 Experimental

Before the distribution experiments, the densities of the solutions were determined to be used. For all experiments, solution volumes were precisely determined from their weight and density, and thus only the statistical error in γ- and X-ray counts was taken into consideration. Meanwhile, HCl concentrations were determined by titration with standardized NaOH solution after γ- and X-ray measurement.

2.2.1.1 Preparation of Radioisotope Tracers ^{88}Zr, ^{175}Hf, and ^{234}Th

The Carrier-free radiotracers of ^{88}Zr ($T_{1/2}$ = 83.4 d) and ^{175}Hf ($T_{1/2}$ = 70.0 d) were produced in the $^{89}\mathrm{Y}(p,2n)^{88}\mathrm{Zr}$ and $^{175}\mathrm{Lu}(p,n)^{175}\mathrm{Hf}$ reactions, respectively, using the AVF cyclotron at the RCNP, Osaka University. To produce ^{88}Zr, approximately 200 mg of Y_2O_3 was irradiated with a 22-MeV ^{1}H (proton) beam with an intensity of 1–2 μA for about 1 h. For the production of ^{175}Hf, approximately 200 mg of Lu_2O_3 or approximately 120 mg of Lu metallic foils (0.25-mm thickness) were irradiated with a 14-MeV proton beam for 5–7 h, where beam current was 1–2 μA. The carrier-free radiotracer of ^{234}Th ($T_{1/2}$ = 24.10 d) was obtained as an α-decay daughter nuclide of ^{238}U ($T_{1/2} = 4.468 \times 10^{9}$ y).

The irradiated Y target was dissolved in several mL of hot aqua regia, and the solution was evaporated to dryness. The residue was dissolved in 0.5–2 mL of concentrated HCl and fed onto a column (5 mm i.d. × 2 cm long) containing anion-exchange resin (Muromac 1 × 8 200–400 mesh Cl^- form). The Y species (containing ^{88}Y, daughter nuclide of ^{88}Zr) was eluted with 3–5 mL of concentrated HCl, while the Zr species was adsorbed on the resin. Subsequently, the Zr species was eluted with 4–5 mL of 4 M HCl. This anion-exchange procedure was repeated again.[61] The ^{88}Zr tracer was stocked with several mL of 4, 6, and 11 M HCl in the PP tubes.

The ^{175}Hf nuclide was purified using a same manner of the purification method of ^{88}Zr nuclide. The irradiated Lu target was dissolved in several mL of a hot aqua regia and the solution was evaporated to dryness. The residue was dissolved in 0.5–2 mL of concentrated HCl and fed onto a column (5 mm i.d. × 2 cm long) containing an anion-exchange resin. The Lu species was eluted with 3–5 mL of concentrated HCl, while the Hf species was adsorbed on the resin. Subsequently, the Hf species was eluted with 4–5 mL of 4 M HCl. This anion-exchange chromatographic procedure was repeated again.[61] The ^{175}Hf tracer was stocked with several mL of 4, 6, and 11 M HCl in the PP tubes.

The 1.2 g of $^{nat}UO_2(CH_3COO)_2$ (nat = natural abundance) was dissolved in 5 mL of concentrated HCl. The U species was extracted from this solution with 5 mL of 1 M of TIOA-xylene or -benzene solution by 5-min shaking. After centrifugation, the organic solution was removed. This liquid-liquid extraction was performed 5 times. The aqueous solution was fed onto a column (8 mm i.d. × 3 cm) containing anion-exchange resin. The Th species was eluted, while U species was adsorbed on the resin with several mL of concentrated HCl.[61] The ^{234}Th tracer was stocked with 1 mL of 6 and 11 M HCl.

2.2.1.2 Adsorption of ^{88}Zr, ^{175}Hf, and ^{234}Th on Polypropylene Surfaces

Adsorption of Zr and Hf on the glass in HCl have been previously reported.[14] As the adsorption interferes with the observation of distribution behavior in solid-liquid extraction, the adsorption behaviors of Zr, Hf, and Th on the surfaces of PP tubes were investigated in a manner similar to references 77 and 78.

The 0.25 mL of 4–11 M HCl containing ^{88}Zr, ^{175}Hf, or ^{234}Th tracer solutions was put in PP tubes at 25 ± 1 °C for 10s–9d. After the requisite time, 0.20 mL of the solution was pipetted into another PP tube, and the sample was subjected to γ-ray (^{88}Zr: E_γ = 392.9 keV, ^{175}Hf: E_γ = 343.4 keV, ^{234}Th: E_γ = 92.4 keV) measurement using a Ge detector. Radioactivities of the samples in 6, 8, and 11 M HCl with the elapsed time of 0 s were defined as the standard radioactivities (A_0). The adsorption ratio (R) on PP surface was evaluated by the equation:

$$R = \frac{A_t}{A_0} , \tag{2-1}$$

where A is radioactivity and the subscript "t" represents the elapsed time of t min for the sample. As such, no adsorption corresponds to R = 1, while 100% adsorption indicated by R = 0.

The time dependencies of the R values were investigated in the time range 10s–9d under following condition. The HCl concentrations were carried for 3.9, 5.7, and 11.0 M HCl for Zr, 3.7, 6.2, and 11.0 M HCl for Hf, and 6.8, 8.5, and 10.9 M HCl for Th.

2.2.1.3 Extraction of ^{88}Zr, ^{175}Hf, and ^{234}Th

The Aliquat 336 resins were prepared in a similar manner to that described in references 41 and 61. The inert support material was MCI GEL CHP20/P30 (Mitsubishi Chemical) with a particle size of ~30 μm. The support material was washed twice alternately with methanol and acetone, and then dried at 110 °C in a vacuum oven. The Aliquat 336 in methanol and the resin were mixed and the mixture was stirred hermetically for about 12 h. After evaporating the methanol at room temperature, the obtained Aliquat 336 resin was dried at 80 °C in a vacuum oven to a constant weight. The weight percentage of Aliquat 336 in the Aliquat 336 resin was determined from the weight of the dried Aliquat 336 resin and the initial weight of the inert support material used. The prepared Aliquat 336 resin was then stored in a desiccator.

The 0.57–15 mg of the 28 wt% Aliquat 336 resin and 0.25 mL of 6–11 M HCl containing the ^{88}Zr, ^{175}Hf, and ^{234}Th tracer solutions were in a PP tube and shaken at 25 ± 1 ºC for 10s–1d using the shaker (M&S Instrument Inc., VORTEX-GENIE2). After 1-min centrifugation using the centrifugal PP filter units (Ultrafree-MC), the resin was separated from the solution phase. The solution phase was pipetted into another tube, and was subjected to γ-ray measurement using the Ge detector. The ratio of the concentrations of the elements between the resin and the solution phases (Q_d) in mL g^{-1} was evaluated by the following equation:

$$Q_\mathrm{d} = \frac{A_\mathrm{r} V_\mathrm{s}}{A_\mathrm{s} W_\mathrm{r}}, \qquad (2\text{-}2)$$

where V and W are the volume (mL) of solution and the mass of the dry resin (g), respectively. The subscripts “r” and “s” denote the resin and solution phases, respectively. The A_r was obtained by subtracting the A_s from the average of A_t.

To examine the time required to equilibrium in the extraction, the time dependences of the Q_d values were studied in the range 10s–1d under following condition. With 28 wt% Aliquat 336 resin, the HCl concentrations were carried for 6.5, 8.7, and 10.9 M HCl for Zr and Hf, and 6.6 and 11.3 M

HCl for Th. Hereafter, the Q_d value in equilibrium is described as the K_d value in distribution reaction. Based on these results, the K_d values of Zr, Hf, and Th were determined in various HCl concentrations with shaking times of at least 4 h. The HCl concentrations in the range 6.5–11.3 M were used in the extraction using 28 wt% Aliquat 336.

2.2.2 Results and Discussion

2.2.2.1 Adsorption on Polypropylene Surface

The dependence of the *R* values of Zr, Hf, and Th on the elapsed time are shown in Figures 2-1(a)–(c), respectively. For all the elements, the *R* values were constant at ~1 in all the HCl concentrations and in the time range studied. In this study, experiments of these elements were carried out using PP tubes, because adsorption of Zr and Hf on the glass in HCl have been previously reported.[14] This indicates negligible adsorption of Zr, Hf, and Th on the PP surface. As a result, it is evident that influence of the adsorption of the group 4 elements on the PP surfaces is negligible in the present extraction experiments for presently purified RI tracers, which indicates that the accurate distribution behavior of Zr, Hf, and Th were examined in this experiment.

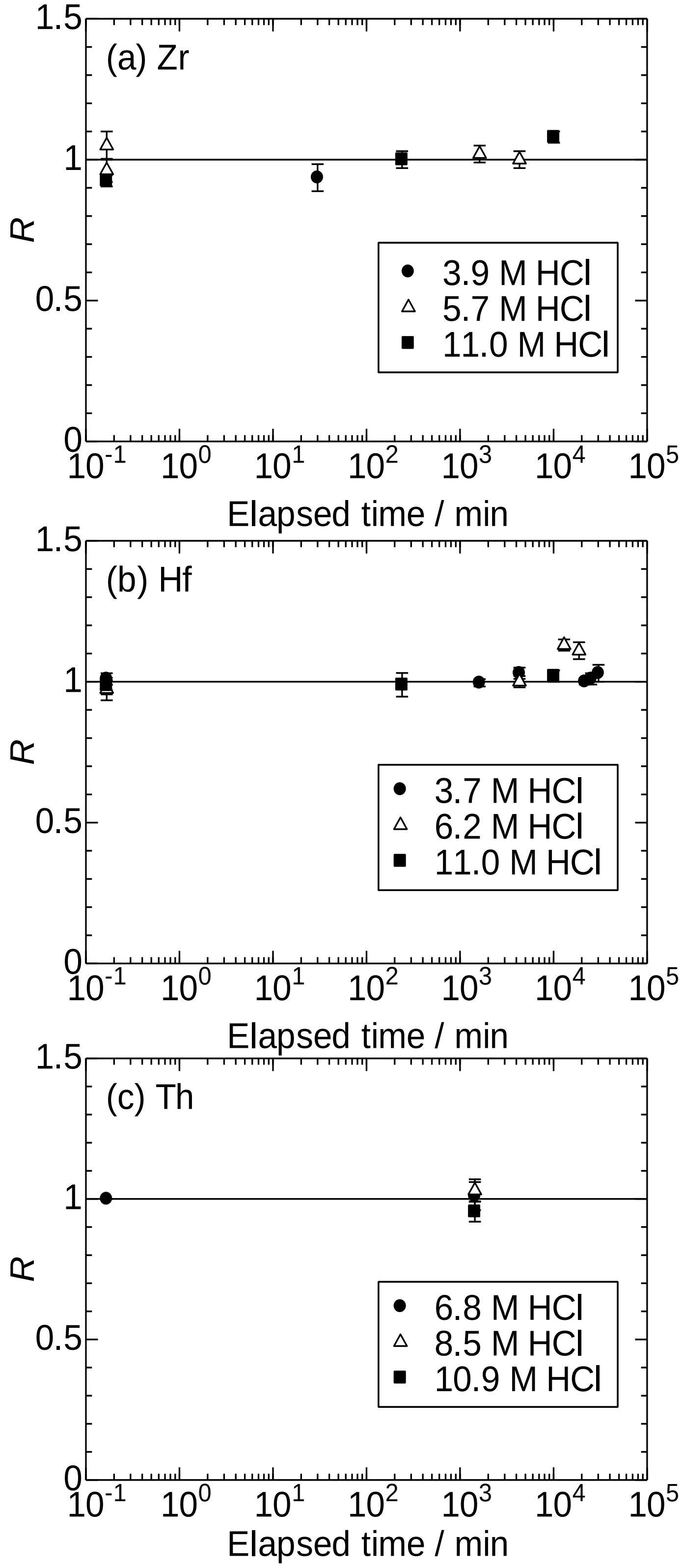


Figure 2-1. The *R* values of (a) Zr, (b) Hf, and (c) Th for different elapsed times in various HCl concentrations. As such, no adsorption corresponds to *R* = 1 (horizontal line), while 100% adsorption indicated by *R* = 0.

2.2.2.2 Dependence of Distribution Behavior on Shaking Time

The dependences of the Q_d values of Zr, Hf, and Th on the shaking time in the 28 wt% Aliquat 336 resin solid-liquid extraction experiments are shown in Figures 2-2(a)–(c), respectively. From these figures, it found that the chemical reactions in the extraction with the 28 wt% Aliquat 336 resin reached to equilibrium within 10 s of shaking. The reactions of these elements with Aliquat 336 as well as TIOA[61] were found to be rapid. Therefore, the solid-liquid extraction under the present condition would be suitable for chemical study of ^{261}Rf ($T_{1/2}$ = 68 s). In the solid-liquid extraction of Zr and Hf in the TIOA/HCl system, clearly slower extraction kinetics was observed with the low concentration (18 and 25 wt%) of TIOA resins, and rapid extraction kinetics was observed with high concentration (≥ 31 wt%) of TIOA resins.[61] Therefore, the rapid extraction kinetics was assumed by higher than 28 wt% Aliquat 336 resins. According to these results, the following experiments (dependence of the K_d values on HCl concentration) were carried out with a shaking time of longer than 4 h.

In the liquid-liquid extraction, the extraction reactions of Zr and Hf in the Aliquat 336/HCl system reached equilibrium with ~20 min (Figures A-1(a) and (b) in Appendix 1). In comparison between the solid-liquid and liquid-liquid extractions, chemical reactions in the solid-liquid extraction reach to the equilibrium more rapidly in the solid-liquid extraction, and the same tendency was observed in extraction in the TIOA/HCl system.[61,79]. This might be due to higher Aliquat 336 concentration in the interfacial surface between the resin and the aqueous solution and/or shorter diffusion length between the organic and aqueous phases than that in the liquid-liquid extraction.

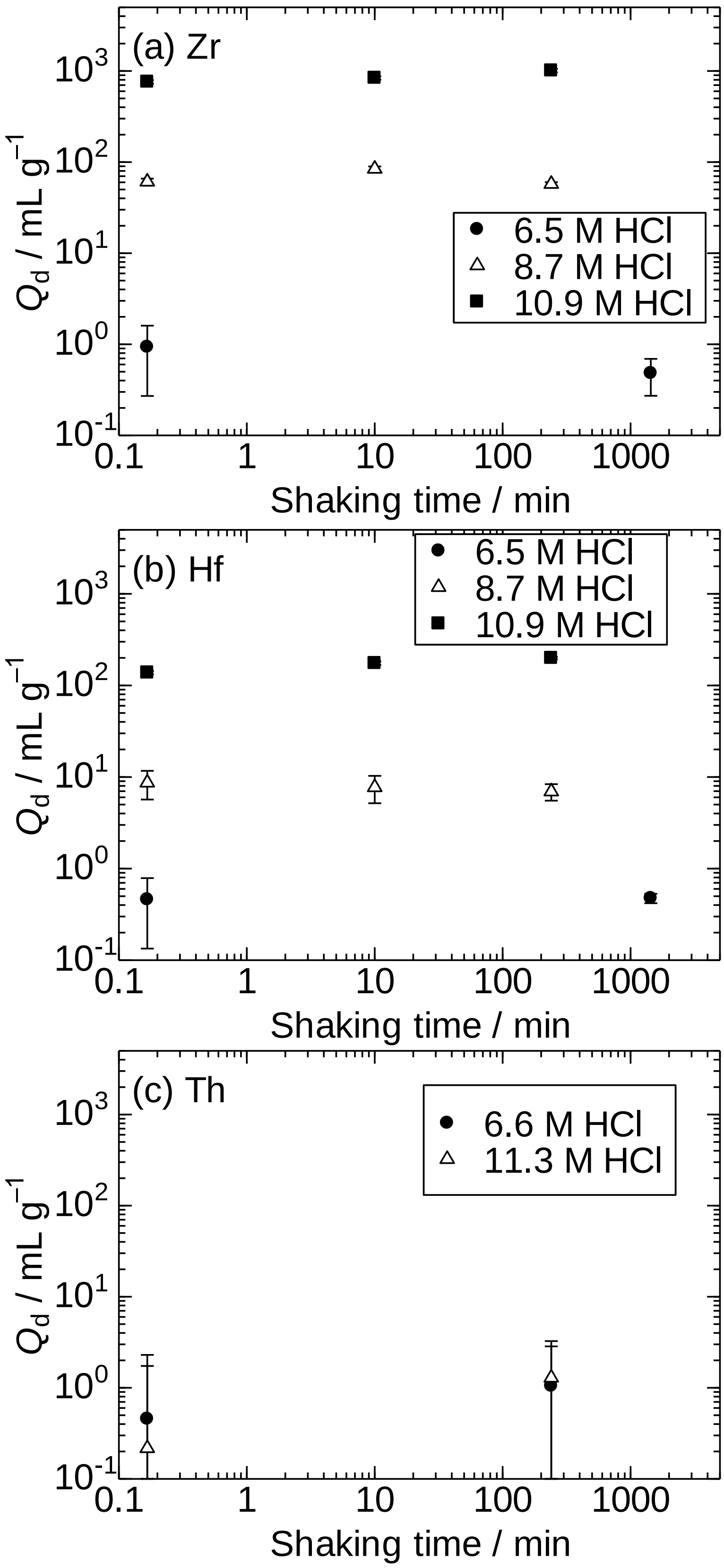


Figure 2-2. The Q_d values of (a) Zr, (b) Hf, and (c) Th for different shaking time in various HCl concentrations with 28 wt% Aliquat 336 resin.

2.2.2.3 Dependence of Distribution Coefficient on HCl Concentration

The dependence of the K_d values of Zr, Hf, and Th on the HCl concentration in the extraction with 28 wt% Aliquat 336 resin is shown Figure 2-3. The K_d values of Zr were small (K_d < 10 mL g^{-1}) in lower than 7.5 M HCl, which indicates that cationic and/or neutral species are dominant in this HCl concentration range. In higher than 7 M HCl, the K_d values of Zr increased with an increase of the HCl concentration, which reflects the formation of the anionic chloride complexes. The extraction behavior of Zr is consistent with those in anion exchange,[40,64,73,74] solid-liquid extraction by amines (Aliquat 336[56,57] and TIOA[61,69]), and liquid-liquid extraction by amines (Primene JM, Amberlite LA-1, Alamine 336, Aliquat 336,[70] and TIOA[76,79]).

For Hf, the K_d values were smaller than 10 mL g^{-1} in lower than 9 M HCl, which indicated that the cationic and/or neutral species were dominantly present under these conditions. In higher than 8.5 M HCl, the K_d values of Hf increased as the HCl concentration increased, indicating that the abundance of the anionic chloride complexes of Hf increases. The extraction behavior of Hf is in agreement with those in anion exchange,[40,64] solid-liquid extraction by amine extractants (Aliquat 336[56,57] and TIOA[61,69]), and liquid-liquid extraction by amine (Primene JM, Amberlite LA-1, Alamine 336, Aliquat 336,[70] Hyamine 1622,[57] and TIOA[79]).

For Th, the K_d values were smaller than 10 mL g^{-1} and constant in all the HCl concentration studied, which indicates that Th does not form anionic chloride complexes and Th dominantly presented as the cationic and/or neutral species under these conditions. This extraction behavior is in agreement with those in anion exchange,[40,73] solid-liquid extraction by amine (TIOA[61]), and liquid-liquid extraction by amines (Primene JM, Amberlite LA-1, Alamine 336, Aliquat 336,[70] and TIOA[76]).

The K_d values were in the sequence of Zr > Hf > Th, which is in agreement with that in the previous reports of anion exchange[40] and solid-liquid extraction by TIOA[61]. The extended X-ray absorption fine structure (EXAFS) spectroscopy studies on Zr and Hf in 8.0–11.9 M HCl suggests that Zr and Hf form anionic chloride complex $[MCl_6]^{2-}$ (M = Zr and Hf).[80] The complex formation reactions are represented as

$$\mathrm{M}^{4+} + n\mathrm{Cl}^{-} \rightleftarrows [\mathrm{MCl}_n]^{4-n} \ (n = 1\text{–}6), \tag{2-3}$$

where n denotes the coordination number in the products. The anionic chloride complexes of $[\mathrm{MCl}_5]^{-}$ and $[\mathrm{MCl}_6]^{2-}$ in equation (2-3) participate in the adsorption–desorption process on the Aliquat 336 resin. The extraction reaction of $[\mathrm{MCl}_6]^{2-}$ is, however, dominant over that of $[\mathrm{MCl}_5]^{-}$ in 8.0–11.9 M HCl. The extraction reaction represent as

$$2\,\overline{\mathrm{QCl}} + [\mathrm{MCl}_6]^{2-} \rightleftarrows \overline{\mathrm{Q}_2[\mathrm{MCl}_6]} + 2\mathrm{Cl}^{-}, \tag{2-4}$$

where QCl indicates Aliquat 336. The equilibrium constant (K_{ex}) derived from equation (2-5) is given by the following equation:

$$K_{\mathrm{ex}} = \frac{\overline{[\mathrm{Q}_2\mathrm{MCl}_6]}[\mathrm{Cl}^{-}]^2}{\overline{[\mathrm{QCl}]^2[\mathrm{MCl}_6{}^{2-}]}}\,. \tag{2-5}$$

The K_{d} value is represented as

$$K_{\mathrm{d}} = \frac{\overline{[\mathrm{Q}_2\mathrm{MCl}_6]}}{\sum_{n=0}^{6}[\mathrm{MCl}_n{}^{4-n}]}\,, \tag{2-6}$$

the stability constant of $[\mathrm{MCl}_6]^{2-}$ (β_6) is

$$\beta_6 = \frac{[\mathrm{MCl}_6{}^{2-}]}{[\mathrm{M}^{4+}][\mathrm{Cl}^{-}]^6}\,, \tag{2-7}$$

from equations (2-5)–(2-7), the following equation is obtained:

$$[\mathrm{Q}_2\mathrm{MCl}_6] = \beta_6 K_{\mathrm{ex}}[\mathrm{QCl}]^2[\mathrm{M}^{4+}][\mathrm{Cl}^{-}]^4\,. \tag{2-8}$$

Therefore, high K_{d} values is indicated affinity of metal and Cl^{-} ions is strong in the same chemical configuration. The K_{d} values of Zr were higher than those of Hf in all HCl concentrations, suggesting that the anionic chloride complexes of Zr would be more stable than those of Hf. The present extraction experimental result reasonably reflect the structural change of the complexes deduced previous EXAFS spectroscopic study.[80] In this study, the comparison data to discuss Rf-chloride complex formation were obtained.

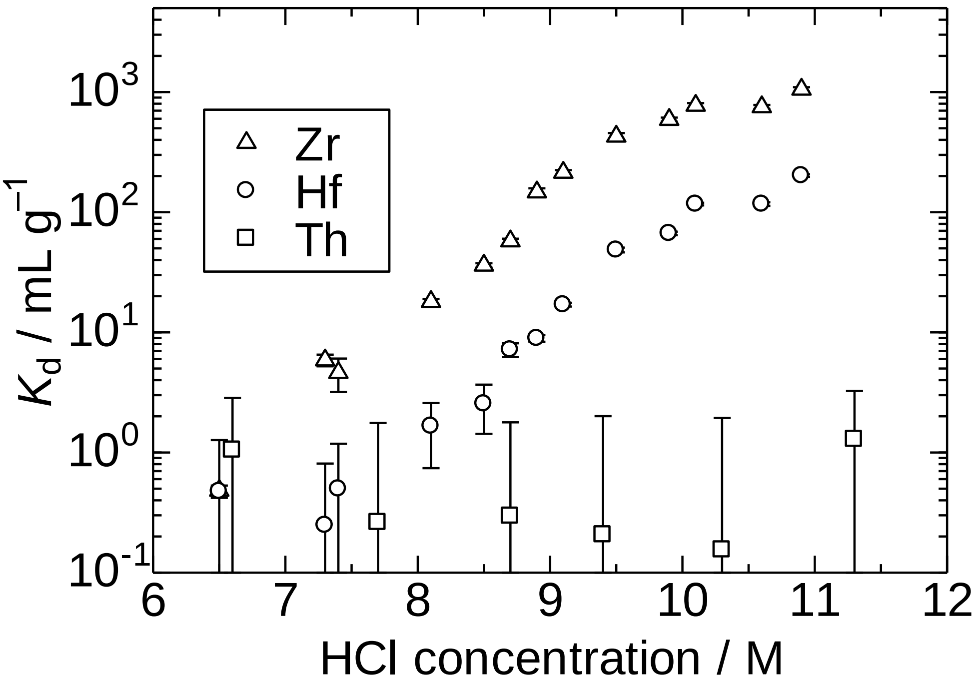


Figure 2-3. 28 wt% Aliquat 336 樹脂を用いたときの Zr, Hf, Th の K_d の HCl 濃度依存性.

2.3 Distribution Experiment of Nb, Ta, and Pa in Cation Exchange and Solid-liquid Extraction by Aliquat 336 from HCl

2.3.1 Experimental

2.3.1.1 Production of Radioisotope Tracers, Nb, Ta, and Pa

The carrier-free radiotracers of ^{95}Nb ($T_{1/2}$ = 34.97 d) and ^{177,179}Ta ($T_{1/2}$ = 56.56 h, 665 d) were produced in the ^{nat}Zr(p,xn)^{95}Nb and ^{nat}Ta(p,xn)^{177,179}Ta reactions, respectively, using the AVF cyclotron at RCNP. The target assembly was constructed with 2 sheets of Zr metal foil (0.05 mm thickness) and 2 sheets of Hf metal foil (0.05 mm thickness) placed downstream of the beam. The targets were irradiated with a 22-MeV proton beam with an intensity of about 1–2 μA for 5–8 h. The carrier-free radiotracer of ^{233}Pa ($T_{1/2}$ = 27.0 d) nuclide was obtained as an α-decay daughter nuclide of ^{237}Np ($T_{1/2}$ = 2.144 × 10^{6} y).

The nuclides were purified using a partially modified version of a procedure found in the reference 77. The irradiated Zr foils were dissolved in 0.4 mL of concentrated HF in a PTFE beaker, and the solution was evaporated to dryness. The residue was dissolved in 2 mL of 1 M HF and fed onto a column (5 mm i.d. × 2 cm long) containing an anion-exchange resin (F^- form). The byproducts and Zr species were eluted with 2 mL of 1 M HF and then with 4 mL of 9 M HCl/0.04 M HF, while Nb species was adsorbed on the resin. Subsequently, the Nb species was eluted with 4 mL of 5 M HNO_3/0.2 M HF. This anion-exchange chromatographic procedure was repeated again. The eluent containing Nb was evaporated to dryness and the residue was dissolved in 2 mL of concentrated HCl, which was followed by the addition of about 120 mg of H_3BO_3. Then, the solution was fed onto another column (5 mm i.d. × 2 cm long) containing the anion-exchange resin (Cl^- form). The fluoride ion was removed from the column with 8 mL of concentrated HCl.[51] The Nb species was then eluted with 6 mL of 1 M HCl. The ^{95}Nb tracer solution was stocked with 1 M HCl in a PP tube.

The irradiated Hf foils were dissolved in 0.4 mL of concentrated HF in a PTFE beaker, and the solution was evaporated to dryness. The residue was dissolved in 3 mL of 1 M HF and fed onto a column (5 mm i.d. × 1 cm long) containing an anion-exchange resin (F^- form). The byproducts and Hf (containing ^{175}Hf, daughter nuclide ^{175}Ta) were eluted with 1 mL of 1 M HF, 6 mL of 9 M HCl/0.04 M HF, and 6 mL of 5 M HNO_3/0.2 M HF, while Ta was adsorbed on the resin. Subsequently, the Ta species was eluted from the column with 6 mL of 1 or 4 M HCl. This procedure was repeated again. The eluent containing Ta was evaporated to dryness and the residue was dissolved in 3 mL of concentrated HCl, which was followed by the addition of about 160 mg of H_3BO_3. Then, the solution was fed onto another column (5 mm i.d. × 4 cm long) containing the anion-exchange resin (Cl^- form). The fluoride ion was removed with 6 mL of concentrated HCl.[51] The Ta species was then eluted with 4 mL of 1 or 4 M HCl. The ^{177,179}Ta tracer solution was stocked with 1 or 4 M HCl in a PP tube.

The ^{237}Np containing ^{233}Pa in HNO_3 was evaporated to dryness in a PTFE beaker. The residue was dissolved in 3 mL of 6 M HCl and was fed onto a column (5 mm i.d. × 2 cm long) containing an anion-exchange resin (Cl^- form). The Pa species was eluted from the column with 4 mL of 9 M HCl/0.025 M HF, while Np species was adsorbed on the resin. Subsequently, the Np species was eluted with sequential washing of 2 M HNO_3 and distilled water. This procedure was repeated again. The eluent containing Pa was evaporated to dryness and the residue was dissolved in 3 mL of 6 M HCl, which was followed by the addition of about 100 mg of H_3BO_3. Then, the solution was fed onto another column (5 mm i.d. × 2 cm long) containing the anion-exchange resin (Cl^- form). The fluoride ion was removed with 5 mL of 6 M HCl.[51] The Pa species was then eluted with 4 mL of 1 M HCl. The ^{233}Pa tracer solution was stocked with 1 M HCl in a PP tube.

2.3.1.2 Adsorption on Polypropylene Surfaces

Adsorption of Nb and Ta on the glass, platinum, and Teflon in HCl have been previously reported.[14] Meanwhile, adsorption of Pa on the glass was reported to become stronger as H^+ and TTA concentrations decreased for liquid-liquid extractions in TTA/toluene/Na^+/H^+/ClO_4^- system.[87] As the adsorption interferes with the observation of distribution behavior in ion exchange and extraction, the adsorption behaviors of Nb, Ta, and Pa on the surfaces of PP tube were investigated.

The 0.5 or 1 mL of 0.1–11 M HCl containing ^{95}Nb, ^{177,179}Ta, or ^{233}Pa tracer solutions was put in a PP tubes at 25 ± 1 °C for 10s–9d. After the requisite time, 0.45 or 0.70 mL of the solution was pipetted into another PP tube, and the sample was subjected to γ- (^{95}Nb: E_γ = 765.8 keV, ^{177}Ta: E_γ = 112.9 keV, ^{233}Pa: E_γ = 312.2 keV) or X-ray (^{179}Ta: E_X = 55.8 keV) measurement using a Ge detector. Radioactivities of the samples in 0.1, 1, 5, and 11 M HCl with the elapsed time of 0 s are defined as the A_0. The R value was determined by equation (2-1).

The time dependencies of the R values were investigated in the range 10s–9d under following condition. The HCl concentrations were carried for 0.098, 1.1, 3.4, 6.1, 8.6, and 10.5 M HCl for Nb, 0.18, 0.68, 1.3, 2.2, 4.3, 5.8, 8.1, and 10.8 M HCl for Ta, and 0.18, 0.68, 1.3, 2.2, 4.3, 5.8, 8.1, and 10.8 M HCl for Pa.

2.3.1.3 Cation-Exchange Adsorption

Cation-exchange resin used was DOWEX 50W × 8 (200–400 mesh, H^+ form). The resin was stirred 5 times alternately with 4 M HCl and 4 M NaOH solutions and was finally converted to H^+ form by a final wash with 4 M HCl. The resin was then washed with distilled water until a neutral solution was obtained, which was followed by drying at 110 °C in a vacuum oven until a constant weight was obtained.[47] The dried resin was then kept in a desiccator until used.

The 16–182 mg of the cation-exchange resin and 1 mL of 0.080–10.9 M HCl containing ^{95}Nb, ^{177,179}Ta, or ^{233}Pa tracer solutions were in a PP tube and shaken at 25 ± 1 °C for 10 s–1 d using the shaker. After 1-min centrifugation, 0.70 mL of the solution was transferred to a PP tube, and was subjected to γ- or X-ray measurement using Ge detector. The Q_d value in mL g^{-1} was evaluated to the equation (2-2).

To examine the time required to equilibrium in the cation-exchange reactions, the time dependences of the Q_d values were studied in the range 10 s−1 d under following condition. The HCl concentrations of 0.27, 0.75, and 1.2 M for Nb, 0.20, 0.42, 0.68, 1.3, and 10.8 M for Ta, and 0.12, 0.30, 0.60, and 1.0 M for Pa. Based on these results, the K_d values of Nb, Ta, and Pa were determined in various HCl concentrations with shaking time of 0.5 d for Nb and Pa or 1 d for Ta. The HCl concentrations in the range 0.080–10.9 M were used.

2.3.1.4 Solid-Liquid Extraction with Aliquat 336 Resin

The 15–48 wt% Aliquat 336 resin were prepared in a manner similar to Subsection 2.2.1.

The 2.1–37.5 mg of the 15–48 wt% Aliquat 336 resin and 0.25 mL of 0.10–10.9 M HCl containing the ^{95}Nb, ^{177,179}Ta, or ^{233}Pa tracer solutions were in a PP tube and shaken at 25 ± 1 °C for 10s–1d using the shaker After 1-min centrifugation using the centrifugal PP filter units, the resin was separated from the solution phase. The solution phase was pipetted into another tube, and was subjected to γ- or X-ray measurement using the Ge detector. The Q_d value was evaluated by equation (2-2).

To examine the time required to equilibrium in the extraction reaction, the time dependences of the Q_d values were studied in the range 10s–1d under following conditions. With 20 wt% Aliquat 336 resin, the HCl concentration were carried for 4.5, 6.5, 9.0, and 10.7 M for Nb, 4.6, 7.8, and 10.9 M for Ta, and 4.6, 5.8, and 10.7 M for Pa. With 48 wt% Aliquat 336 resin, the HCl concentrations were 3.8, 8.1, and 10.1 M for Nb, 3.7, 6.2, and 10.8 M for Ta, and 3.6, 6.1, 10.0 M for Pa. Based on these results, the K_d values of Nb, Ta, and Pa were determined in various HCl and Aliquat 336 concentrations with shaking time of 4 h for Nb and Pa or 24 h for Ta. The HCl concentrations in the range 1.2–10.9 M were used in the extraction using 20 wt% Aliquat 336, while the HCl concentrations in the range 0.10–10.9 M were used in the extraction using 48 wt% Aliquat 336. In addition, the HCl concentration was kept constant at 6, 8, and 10 M HCl, and the Aliquat 336 wt% was varied for 15–48 wt%.

2.3.2 Results and Discussion

2.3.2.1 Adsorption on Polypropylene Surfaces

The dependences of the *R* values of Nb, Ta, and Pa on the elapsed time are shown in Figures 2-4(a)–(c), respectively. For all the elements, the *R* values were constant at ~1 in all the HCl concentrations and in the time range studied, indicating negligible adsorption under the employed conditions. Though, inconsistent distribution behaviors were reported among some experiments. Adsorption on the container surface caused by problem of purification would be one of reason for inconsistencies. In this work, purification methods of RI tracers were previous method[77] and multistep. As a result, it is evident that influence of the adsorption of the group 5 elements on the PP surfaces is negligible in the present cation-exchange and extraction experiments for presently purified RI tracers, which indicates that the accurate K_d values of Nb, Ta, and Pa were examined in this experiment.

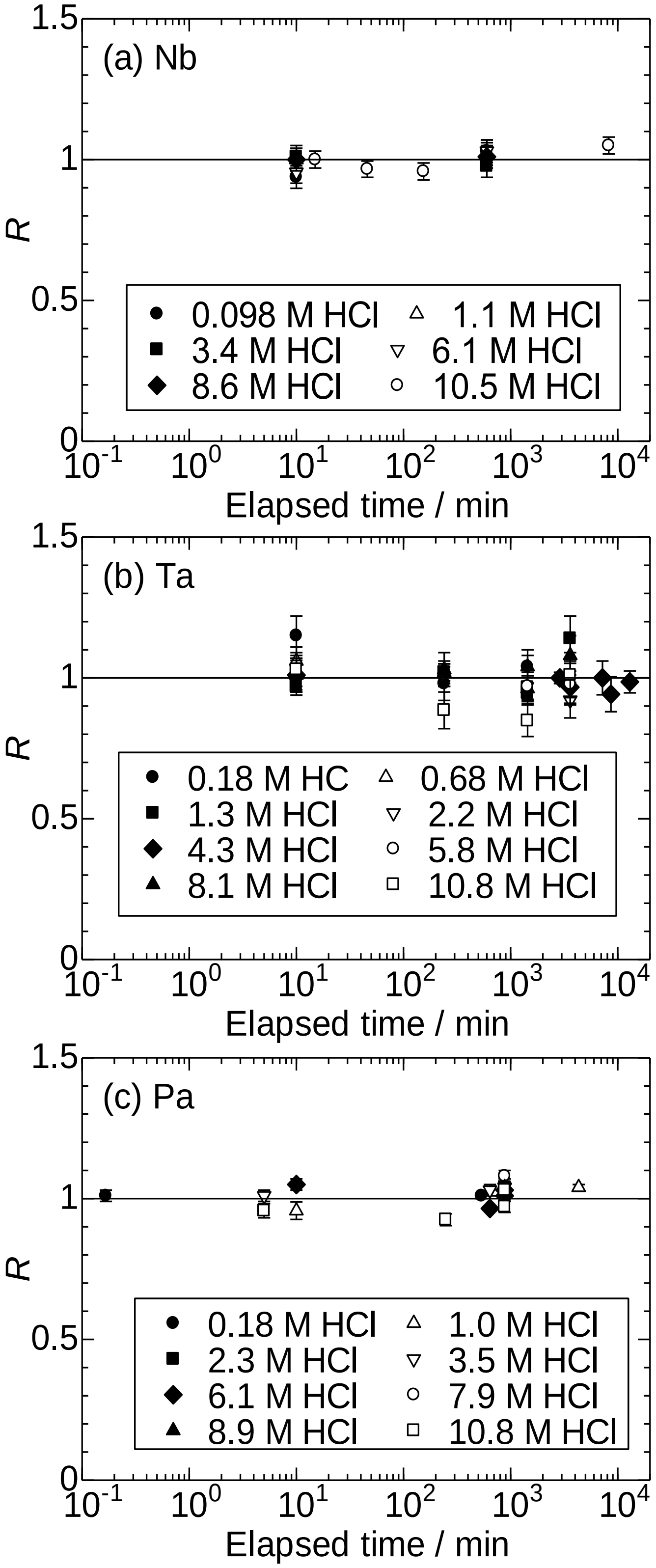


Figure 2-4. The *R* values of (a) Nb, (b) Ta, and (c) Pa for different elapsed times in various HCl concentrations. As such, no adsorption corresponds to *R* = 1 (horizontal line), while 100% adsorption indicated by *R* = 0.

2.3.2.2 Dependence of Distribution behavior on Shaking Time

The dependences of the Q_d values of Nb, Ta, and Pa on the shaking time in the cation exchange are shown in Figures 2-5(a)–(c), respectively. The Q_d values remain roughly constant for all experiments, indicating that equilibrium was established within 10 s. Therefore, the solid-liquid extraction under the present condition would be suitable for chemical study of ^{262}Db despite its 34-s half-life.

In the solid-liquid extraction with 20 wt% Aliquat 336 resin, the dependencies of the Q_d values of Nb, Ta, and Pa on the shaking time are shown in Figures 2-6(a)–(c), respectively; the corresponding data with the 48 wt% Aliquat 336 resin are shown in Figures 2-6(d)–(f). The Q_d values of Nb and Pa became constant in 10-s shaking for all the HCl concentrations, suggesting that the reactions of Nb and Pa with chloride and the solid-liquid extraction are fully rapid to reach equilibria. In contrast, the Q_d values of Ta became constant after 2–3 h in all the HCl concentrations studied. In the liquid-liquid extraction in this reaction system, the extraction kinetics of Nb and Pa was also fast and that of Ta was slow (Figures A2-2(a) –(f) in Appendix 2). Ion-pair extraction systems operate through several reactions:

$$\mathrm{M}^{n+} + m\mathrm{X}^{-} \leftrightarrows [\mathrm{MX}_m]^{l-}, \tag{2-9}$$

$$[\mathrm{MX}_m]^{l-} + l\mathrm{QY} \leftrightarrows \mathrm{Q}_l[\mathrm{MX}_m] + l\mathrm{Y}^{-}, \tag{2-10}$$

$$\mathrm{Q}_l[\mathrm{MX}_m]_\mathrm{s} \leftrightarrows \mathrm{Q}_l[\mathrm{MX}_m]_\mathrm{r}. \tag{2-11}$$

M^{n+}, X^{-}, and QY represent metallic cation, anionic ion, and ion-pair extractant, respectively. Reactions (2-9), (2-10), and (2-11) are the formation of the complex metal ion, formation of the ion-pair complex, and distribution of that complex, respectively. Reaction (2-4) is essentially electrostatic in nature and is rapid and highly reversibly.[88] This suggests that reactions (2-3) and/or (2-5) are slower for Ta than are for Nb and Pa. It was expected that the distribution reaction is shortened by using a smaller resin particle size and/or by raising the temperature.[78,89]

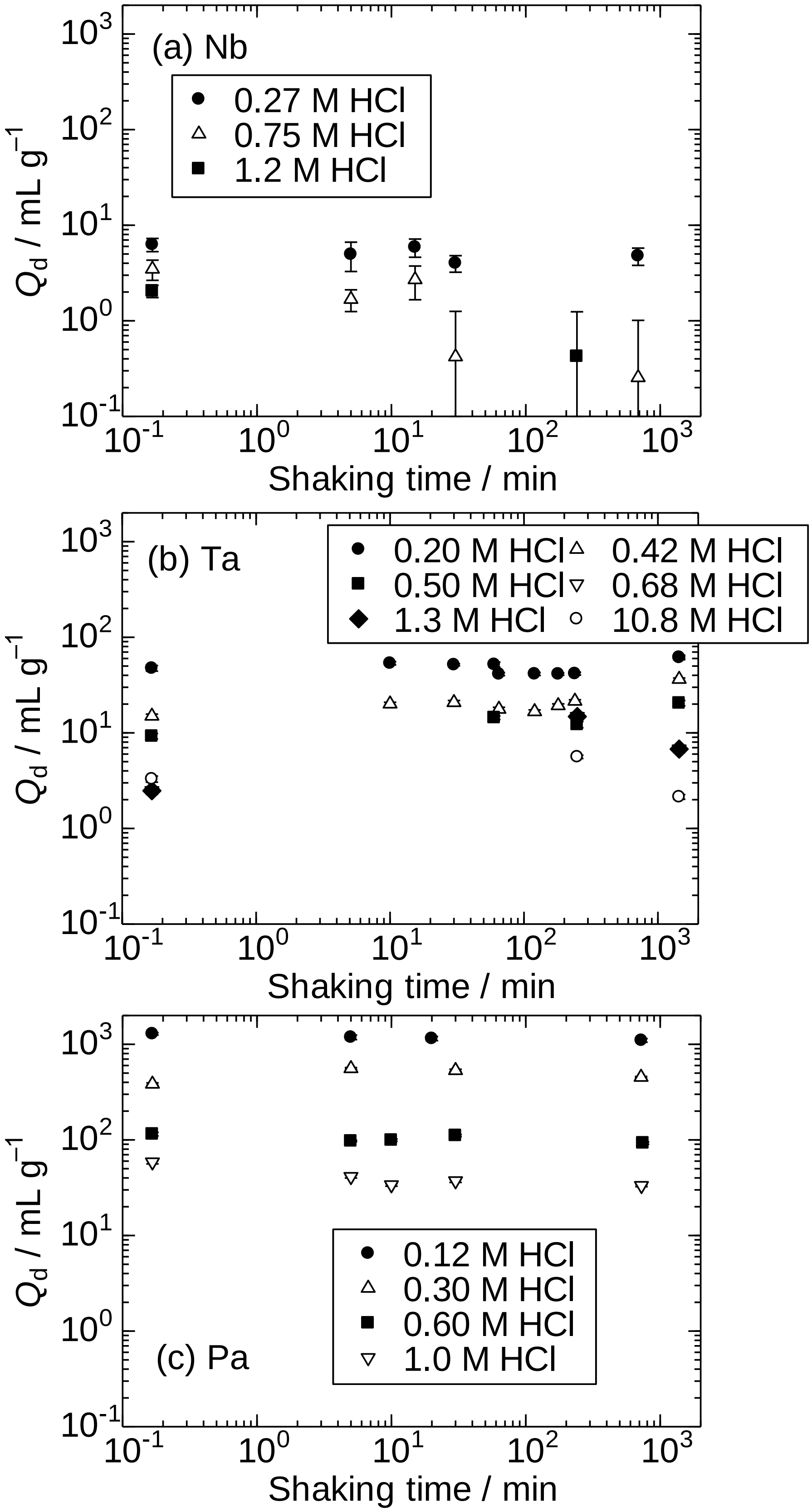


Figure 2-5. The Q_d values of (a) Nb, (b) Ta, and (c) Pa for different shaking times in various HCl concentrations during cation exchange.

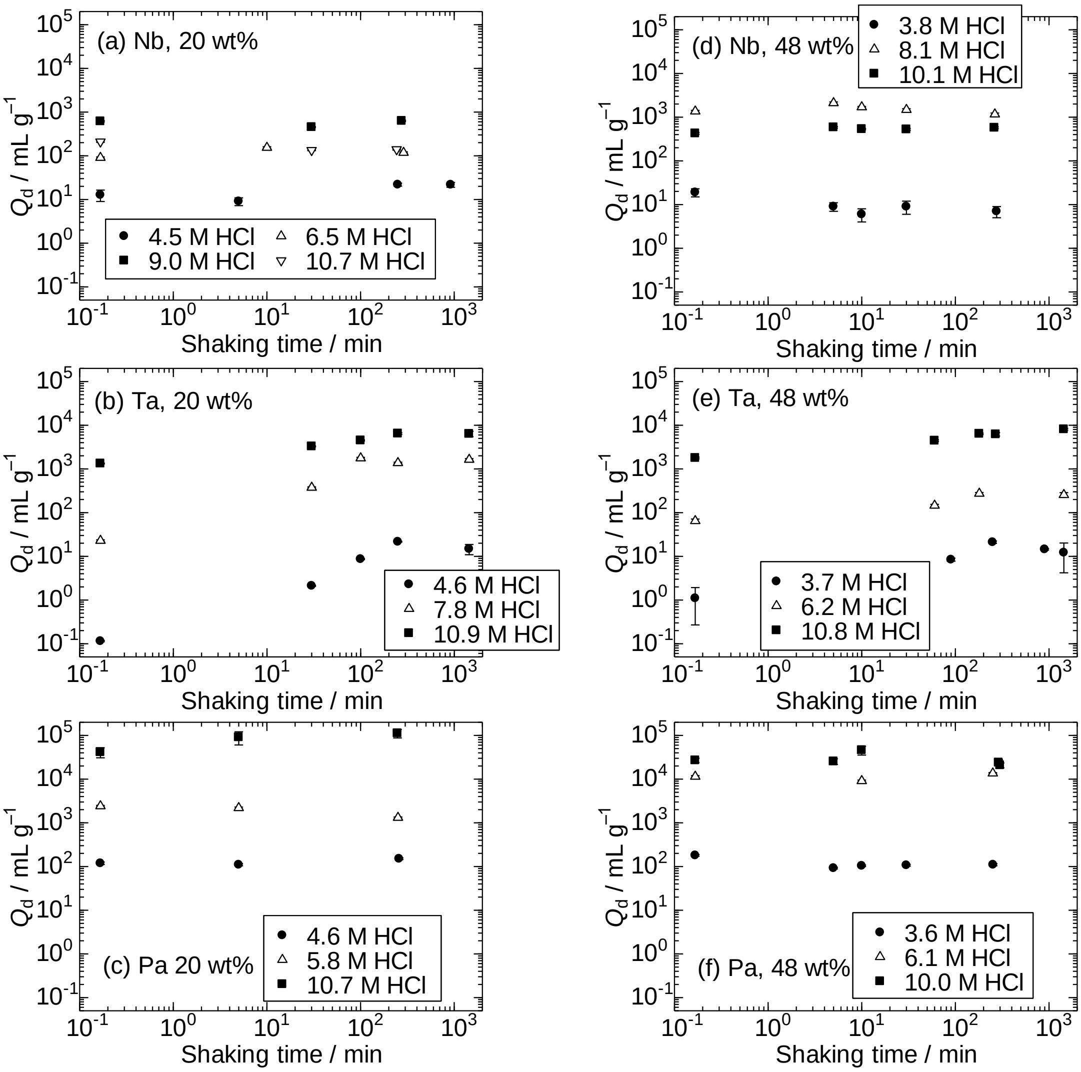


Figure 2-6. The Q_d values of (a), (d) Nb, (b), (e) Ta, and (c), (f) Pa for different shaking times in various HCl concentration with (a)–(c) 20 wt% and (d)–(f) 48 wt% Aliquat 336 resins.

2.3.2.3 Dependence of Distribution Coefficient on HCl Concentration

The dependences of the K_d values of Nb, Ta, and Pa on the HCl concentration in the cation exchange are shown in Figure 2-7. The corresponding values in ≤ 0.1 M HCl is shown in the inset of Figure 2-7. In the solid-liquid extraction with 20 wt% and 48 wt% Aliquat 336 resins, the K_d values of those elements on the HCl concentration are shown in Figures 2-7(a) and (b), respectively.

In the cation-exchange experiment, the K_d values of Nb were smaller than 20 mL g^{-1} and constant regardless of HCl concentration, which indicates that the neutral and/or anionic species were dominantly present under these conditions; this behavior is in agreement with previous results.[90,91] In the extraction by Aliquat 336, lower K_d values for Nb at HCl concentrations lower than 4 M indicate low concentration of the anionic Nb species, suggesting that the neutral species $[Nb(OH)_2Cl_3]$[72,85,92] and/or $[NbOCl_3]$[85] are dominant. Note that these values increased with the HCl concentration, reflecting formation of the anionic species $[Nb(OH)_2Cl_4]^-$,[72,85,92] $[NbOCl_4]^-$,[85] and/or $[NbOCl_5]^{2-}$.[84] This behavior is in agreement with those observed in previous experiments employing anion exchange,[64,73,74] solid-liquid extraction by amine extractants (triisooctylamine[69] and Aliquat 336[56,57]) and liquid-liquid extraction by amine extractants (methyldioctylamine,[65] tribenzylamine,[66,72] Primene JM, Amberlite LA-1, Alamine 336, Aliquat 336,[70] trioctylamine,[70,75] and triisooctylamine[68,76]). The K_d values of Nb increased with an increase of the HCl concentration to 8 M; after this point, those values decreased. The presence of the cationic species $[Nb(OH)Cl_3]^+$ was reported for high concentration of H^+ and low concentration of Cl^-;[92] as such, assuming that $[Nb(OH)Cl_3]^+$ did not form in this experiment, because the H^+ and Cl^- concentrations were fairly constant and the K_d values for cation exchange were fairly small ($K_d \leq 20$ mL g^{-1}) for high HCl concentrations. This means that the Nb anionic species contain ligands capable of protonation; these can be accounted for by either hydrooxo chloro[72] or oxo chloro complexes. Note that the observed behavior differs from previous anion-exchange experiments[73,74,90] and trioctylamine-mediated liquid-liquid extraction,[71] which reported high K_d values and extraction yields of Nb for low concentration of HCl.

For Ta, the K_d values in the cation-exchange experiment were ~10^2 mL g^{-1} in 0.1 M HCl and decrease as HCl concentration increased to 2 M. This reflects the decrease in abundance of cationic Ta through the formation of neutral and/or anionic species, and/or by the influence of H^+ ion as a counterion. The K_d values of Ta were small in 0.5–11 M HCl, which indicates that cationic species are few under these conditions. This cation-exchange behavior is in agreement with the previous result (in ≥ 9 M HCl).[90] In the solid-liquid extraction by Aliquat 336, the K_d values of Ta were small in 0.1–5 M HCl. These results and ones in the cation-exchange adsorption suggest that cationic and neutral species are dominant in 0.08–0.5 M and 0.5–5 M HCl, respectively. In higher than 4 M HCl, the K_d values of Ta increased with an increase of the HCl concentration. This reflects the formation of the anionic species such as $[TaCl_6]^-$.[84,93] This behavior is consistent with previous research reporting on anion exchange,[64] solid-liquid extraction using Aliquat 336[56,57] and liquid-liquid extraction using amine extractants (Hyamine 1622,[67] Primene JM, Amberlite LA-1, Alamine 336, and Aliquat 336[70]). On the other hand, present extraction behaviors are not consistent with those of solid-liquid extraction by triisooctylamine[69] and liquid-liquid extraction by methyldioctylamine,[65] tribenzylamine,[66] which reported small and constant of extraction ratio of Ta in wide range of HCl concentration. Note that the observed differs from previous liquid-liquid extraction by trioctylamine, which reported the extraction yield of Ta were decreased with an increase HCl concentration.[71]

For Pa, the K_d values in the cation-exchange experiments were ~10^3 mL g^{-1} in 0.1 M HCl and decreased as HCl concentrations increased to 2 M. This is accounted for by the fact that Cl^- is non-complexing anion of Pa^{5+} at HCl concentration lower than 1 M,[94] thereby allowing H^+ to act as a counterion. As such, the dominant cationic Pa species at HCl concentrations lower than 1 M have been reported to be $[PaO_2]^+$,[95] $[PaO(OH)]^{2+}$,[94,96] and/or $[PaO(OH)_2]^+$.[96] In addition, the K_d values of Pa remained low and relatively constant all the way up to 11 M HCl, which indicates relatively low levels of cationic species throughout; again, these results are consistent with previous research for HCl concentrations equal to or exceeding 9 M.[90] For solid-liquid extraction by Aliquat 336, the K_d values of Pa were small in the range 0.1–3 M, which indicates only low levels of the anionic species. Previous research in cation-exchange adsorption and Aliquat 336 extraction revealed the dominant Pa species in 2–3 M HCl to be neutral complexes such as $[Pa(OH)_2Cl_3]$,[94,97–99] $[Pa(OH)Cl_4]$,[94,97] and/or $[PaOCl_3]$.[94] Furthermore, the K_d values increased with HCl over 3 M, which reflects the formation of anionic species such as $[\mathrm{Pa(OH)_2Cl_4}]^-$, $[\mathrm{Pa(OH)Cl_5}]^-$, $[\mathrm{PaCl_6}]^-$,[94,97–99] $[\mathrm{PaOCl_4}]^-$,[100] $[\mathrm{PaCl_7}]^{2-}$,[94,97,98] and $[\mathrm{PaOCl_5}]^{2-}$.[94] This extraction behavior is consistent with precious research in anion exchange,[73,99,101,102] solid-liquid extraction using Aliquat 336[56,57] and TEVA resin,[100] and liquid-liquid extraction using Aliquat 336[64] and triisooctylamine.[100,101]

Overall, in the cation exchange, the K_d values were found to be Pa > Ta > Nb; meanwhile, the size of the ionic radii are $\mathrm{Pa^{5+}} > \mathrm{Nb^{5+}} \approx \mathrm{Ta^{5+}}$.[103] The near equivalent of the Nb and Ta ionic radii indicates similar charge densities for complexes with the same chemical configuration. It was assumed that the different cation-exchange behaviors between Nb and Ta are therefore attributed to different chemical conformations, as has been previously reported for cation exchanges in $\mathrm{HF/HNO_3}$.[104] Meanwhile, the K_d values for the Aliquat 336 extractions were found to be Pa > Ta > Nb. The difference might be the result of the fact that protonation of Nb species is more significant in solid-liquid extractions. Again, the difference in distribution behaviors between Nb and Ta are attributed to different chemical configurations, as Nb forms hydrooco and/or oxo chloride complexes[72,84,85,92] while Ta prefers a pure chloride complex.[84,93]

As previously described, the inconsistent distribution behaviors of Nb and Ta are reported among some experiments,[56,57,64–73,75,76] and polymerization,[63] adsorptive property,[14] and non-equilibrium in distribution reactions are considered as the reasons. Although the adsorption interferes with precise determination of distribution behavior, in this work, RI tracers successfully purified and influence of the adsorption of Nb, Ta, and Pa on the PP surfaces was negligible and good reproducibility of the data was observed. The reliable data could be provided in this work. Time dependences of the distribution behaviors of Nb, Ta, and Pa also investigated. For Ta, clearly slower extraction kinetics than Nb and Pa was observed, which would be one of the reasons for these inconsistencies. Indeed, the higher K_d values of Nb than those of Ta were obtained in the short contact time (2 min) of two phases with the aim of Db experiment.[56,57] This is considered to be caused by the slow kinetics of Ta. Of course, in some experiments using macro amounts of atoms, the behaviors of polymers might be observed, resulting in the inconsistent values with those in this work. In the present experiment, carrier-free radiotracers were used to investigate the chemical behaviors of monomeric species which are important to investigate the chemical properties of Db existing as single atoms.

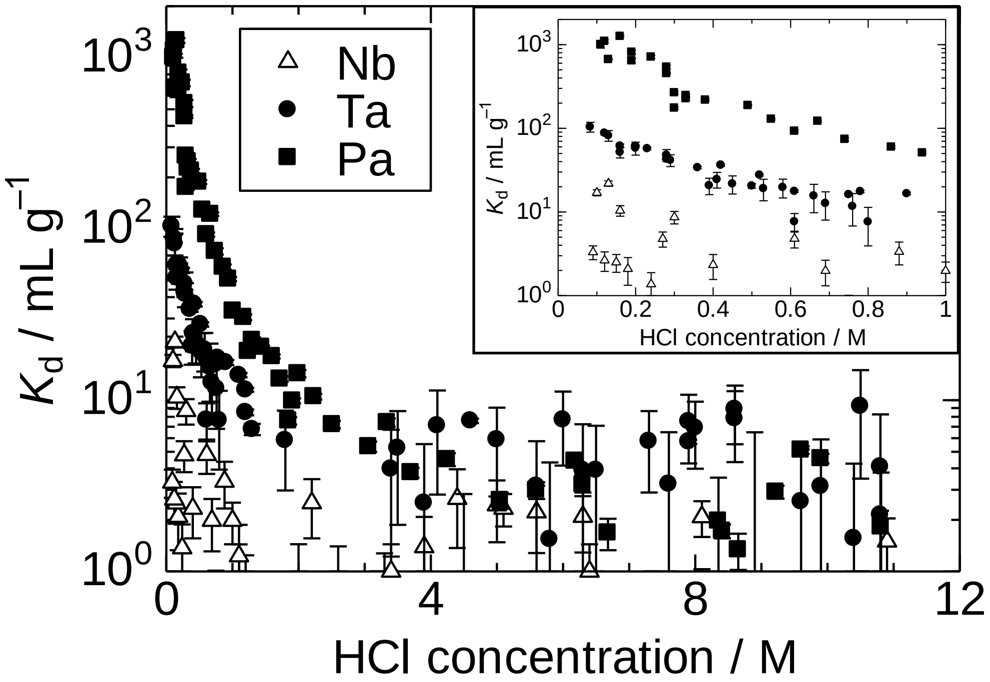


Figure 2-7. The K_d values of Nb, Ta, and Pa as a function of the HCl concentrations during cation exchange.

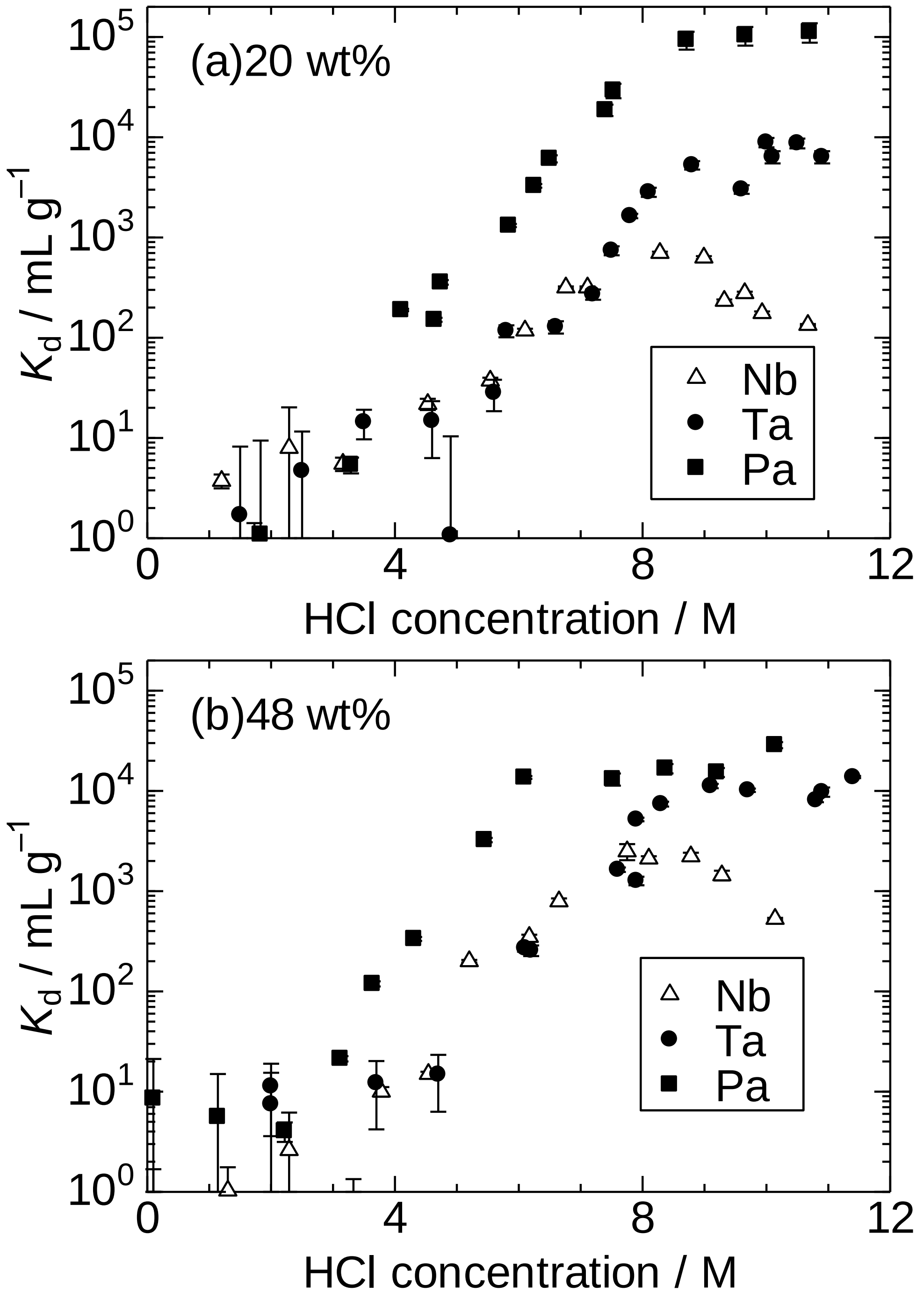


Figure 2-8. The K_d values of Nb, Ta, and Pa as a function of the HCl concentration with (a) 20 wt% and (b) 48 wt% Aliquat 336 resins.

2.3.2.4 Dependence of Distribution Coefficient on Aliquat 336 Concentration

In the liquid-liquid extraction, assuming that Aliquat 336 ($(R_3NCH_3)Cl$) extracts the single species of anionic metallic complex ($[MX]^{n-}$), the extraction equilibrium can be denoted by the following equation:

$$n(R_3NCH_3)Cl_{org} + [MX]^{n-}{}_{aq} \leftrightarrows (R_3NCH_3)_n[MX]_{org} + nCl^{-}{}_{aq}. \tag{2-12}$$

The equilibrium constant (K_{ex}) derived from equation (2-12) is given by the following equation:

$$K_{ex} = \frac{[(R_3NCH_3)_n MX]_{org}[Cl^-]^n{}_{aq}}{[(R_3NCH_3)_n Cl]_{org}{}^n [MX^-]_{aq}} . \tag{2-13}$$

Here, it is assume that the distribution ratio (D) of equation (2-12) is expressed by the equation:

$$D = \frac{[(R_3NCH_3)_n MX]_{org}}{[MX^-]_{aq}} . \tag{2-14}$$

From equations (2-13) and (2-14), the following equation is obtained:

$$\log D = n\log\,[(R_3NCH_3)Cl]_{org} + \log K_{ex} - n\log\,[Cl^-]. \tag{2-15}$$

The increase in the chloride ion concentration by dissociation of the Aliquat 336 is very small compared with the initial chloride ion concentration of the aqueous phase and thus that the value of $[Cl^-]_{aq}$ is assumed to be almost constant through the extraction. Thus, a linear correlation between log D and log [Aliquat 336] is obtained with the slope value corresponding to the net charge of the extracted metallic complex, when the single species of anionic metallic complex is extracted by Aliquat 336. Similar relationship between the slope value and net charge also holds in the solid-liquid extraction.[42,61] In the solid-liquid extraction, log K_d is obtained:

$$\log K_d = n\log\,[(R_3NCH_3)Cl]_{org} + \log K_{ex} - n\log\,[Cl^-]. \tag{2-16}$$

In Figures 2-9(a)–(c), the dependences of the log K_d of Nb, Ta, and Pa, respectively, on the log [Aliquat 336] in the extraction from 6, 8, and 10 M HCl are shown. The log K_d values of all the Nb samples linearly increased with increasing log [Aliquat 336]. For Ta, the linear relationships between log K_d and log [Aliquat 336] values were obtained in 6 M HCl. For Pa, the linear relationships between log K_d or log D and log [Aliquat 336] values were obtained in 6 M HCl. A linear relationships between log K_d and log [Aliquat 336] for Ta and Pa was not obtained in solid-liquid extraction in 8 and 10 M HCl, while good linearities between log D and log [Aliquat 336] for Ta and Pa were observed in liquid-liquid extraction as shown in these concentrations in Figures A2-4(b) and (c) in Appendix 2. This is likely because those K_d values are too high to be accurately determined by the present method.

All available slopes are summarized in Table 2-1. The slope values of Nb under all conditions are ~1. Consequently, the present data indicate that one Aliquat 336 cation is paired with the anionic Nb complex with a net charge of −1 to be extracted into resin phase from 6, 8, and 10 M HCl; this result is consistent with previous work using tribenzylamine-Cl in 10 M HCl.[72] Based on the present data and references 72, 82, and 90, it was proposed $[Nb(OH)_2Cl_4]^-$ [72,85,92] and/or $[NbOCl_4]^-$ [85] for the chemical species of Nb.

Slope value for Ta in 6 M HCl was ~1. In the liquid-liquid extraction, all Ta experiments in 6, 8, and 10 M HCl for which linear slopes were obtained gave values of ~1 (Table A2-1 in Appendix 2). These results indicate that the anionic Ta complex has a net charge of −1. These results are consistent with previous research; according to Raman spectroscopic analysis of Ta for high concentration (≥ 11.4 M) of HCl, Ta ([Ta] = 2.5×10^{-3} M) is exclusively found in $[TaCl_6]^-$.[84,93]

Finally, slope value for Pa in the 6 M HCl was ~1. In the liquid-liquid extraction, slope values in the 6 and 8 M HCl were ~1 (Table A2-1 in appendix 2). This again indicates an anionic complex with a net charge of −1, such as $[Pa(OH)_2Cl_4]^-$, $[Pa(OH)Cl_5]^-$, $[PaCl_6]^-$,[97–99] and/or $[PaOCl_4]^-$.[100] In contrast, the slope value for Pa in previous liquid-liquid extraction in an Aliquat 336/6 M HCl system was 0.58, suggesting the presence of hydrolysis species.[86] The difference between this work and the previous one could be caused by a small difference in HCl concentration, differences in the extracted species between toluene (which has been used in the previous report) and carbon tetrachloride (liquid-liquid extraction study), and/or physical adsorption on the resin. Meanwhile, in the liquid-liquid extraction experiment, the slope values in the 10 M HCl was about 2 (Table A2-1 in

Appendix 2), which indicates an anionic Pa complex with a net charge of −2, such as $[PaCl_7]^{2-}$ [94,97] and/or $[PaOCl_5]^{2-}$.[94] Previous research in 12 M HCl reported a slope of 1.09 in liquid-liquid extraction with TIOA.[100] The net charge of the Pa species decreases from −1 in 6–8 M HCl to −2 in 10 M HCl and then increases from −2 to −1 in 12 M HCl;[100] dominant anionic species of Pa could continually change in this range.

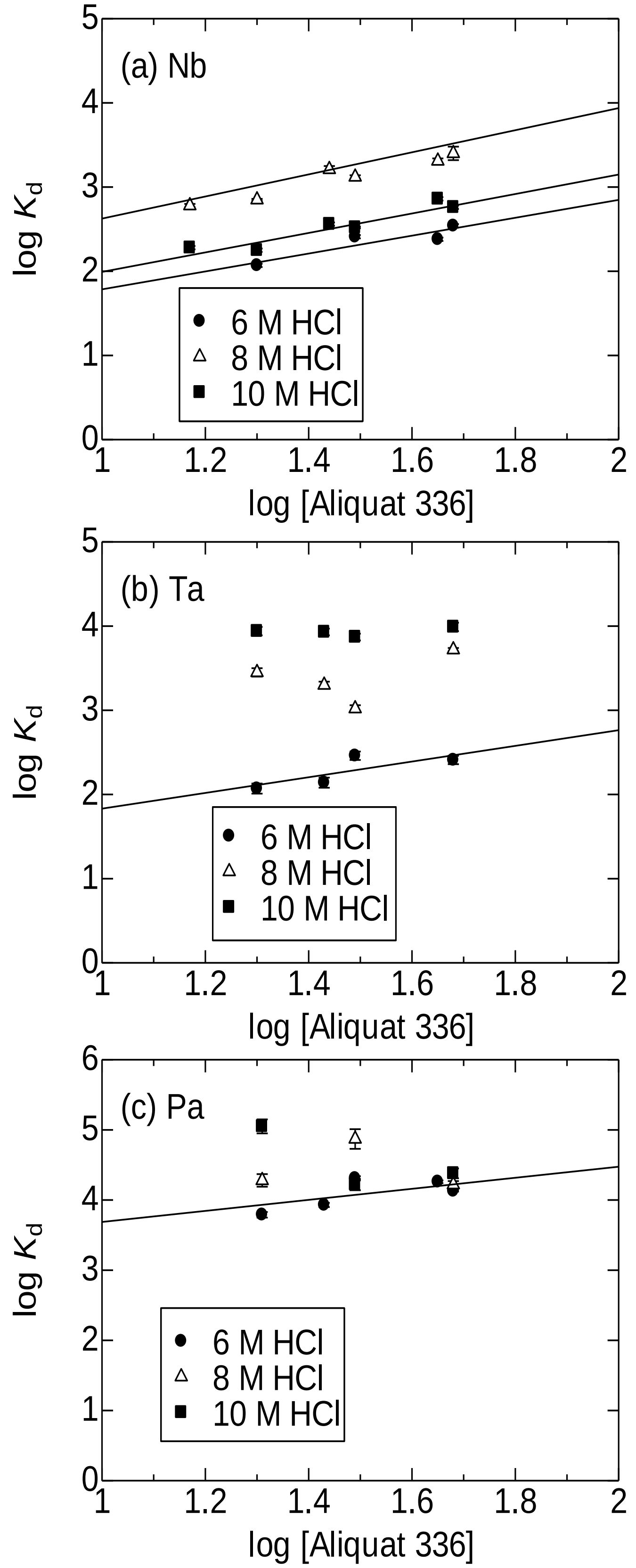


Figure 2-9. The K_d values of (a) Nb, (b) Ta, and (c) Pa as a function of Aliquat 336 weight concentration at the constant HCl concentration of 6, 8, and 10 M HCl.

Table 2-1. Slopes (*s*) of fitted linear lines in Fig. 2-9: log $K_d = s \log [\text{Aliquat 336}] + C$

HCl concentration / M	Slope (*s*)		
	Nb	Ta	Pa
6	1.1 ± 0.1	0.9 ± 0.3	0.8 ± 0.2
8	1.2 ± 0.2	—[a]	—[a]
10	1.2 ± 0.2	—[a]	—[a]

[a] A linear correlation between log K_d and log [Aliquat 336] was not obtained.

2.4 Experimental Conditions for the Chemical Study of Rf and Db

2.4.1 Experimental Conditions for the Chemical Study of Rf Using Solid-Liquid Extraction by Aliquat 336

AMBER[61] will be used in solid-liquid extraction experiment of Rf. The half-lives of ^{261}Rf and its daughter nucleus ^{257}No are 68 [104] and 24.5 s,[82] respectively. The cross section of nuclide ^{261}Rf was 13 nb with ^{248}Cm target at 94 MeV of ^{18}O beam.[20] In the bombardment of 685.2 μg/cm^2 of ^{248}Cm with ^{18}O beam (beam current: 0.8 particle-μA, gas-jet transport efficiency: 50%, chemical yield: 50%, the efficiency of detector: 34%), the event rate in sum total of ^{261}Rf and ^{257}No is estimated to be 208 events/day (cycle time: 133 s, sample preparation time: 87 s, number of cycle: 400 times).

The time dependence of the K_d values of Zr, Hf, and Th showed that extraction reactions reach equilibrium within 10 s of shaking in 6–11 M HCl by 28 wt% Aliquat 336 resin. Therefore, at least higher than 28 wt% Aliquat 336 resin is expected to be suitable for Rf experiments. Although the K_d values determined in the off-line experiment were found in a wide range (6.5–11.3 M HCl), the ratios activities of the resin and solution phases were within the range approximately 0.01–100. Because too high or too low ratios of the activity of events between two phases should be avoided for the determination of the K_d values of transactinides with a small number of events. From such point of view, suitable concentration of HCl for first Rf experiment is 8–10 M in the solid-liquid extraction by 28 wt% Aliquat 336 resin on the assumption that the extraction sequence is Rf > Zr > Hf as reported in anion-exchange experiment using hot HCl (80 ºC)[10,40] and is Zr > Hf > Rf (4–8 M HCl) as reported in theoretical calculation.[49]

2.4.2 Experimental Conditions for the Chemical Study of Db Using Cation-Exchange Adsorption, Solid-Liquid Extraction by Aliquat 336

AMBER[61] will be used for cation-exchange and solid-liquid extraction experiments. The half-lives of ^{262}Db and its daughter nucleus ^{258}Lr are 34 and 3.5 s, respectively. The cross section of the nuclide ^{262}Db was 2.1 nb with ^{248}Cm target at 103.1 MeV of ^{19}F beam.[106] In the bombardment of 685.2 mg/cm^2 of ^{248}Cm with ^{19}F beam (beam current: 0.8 μA, gas-jet transport efficiency: 50%, chemical yield: 50%, the efficiency of detector: 34%), the event rate in of sumb ^{262}Db and ^{258}Lr is estimated to be 8.2 events/day (cycle time: 133 s, sample preparation time: 87 s, number of cycle: 400 times).

The time dependence of the K_d values of Nb, Ta, and Pa showed that cation-exchange reactions reach equilibrium within 10 s of shaking in 0.1–11 M HCl. Therefore, the cation-exchange experiment under the present conditions would be suitable for the chemical study of ^{262}Db ($T_{1/2}$ = 34 s). The difference in cation-exchange behavior between Nb, Ta, and Pa as a result of their different chemical configurations and ionic radii make the question of the cation-exchange behavior of Db an interesting one.

If the Aliquat 336 extraction reaction kinetics of Db is similarly fast to that of Nb and Pa, the present extraction conditions should be suitable for Db. However, if they are similar to those of Ta, the current system will not be fast enough to fast enough to allow for equilibrium. Clearly, it will be necessary to investigate the extraction kinetics of Db in detail to come to any positive determination. A more rapid extraction system might still be required for Ta experiments even if it is not for Db. Because too high or too low ratios of events between two phases should be avoided for the determination of the K_d values of transactinides with a small number of events. From such point of view, it was proposed that suitable concentration of HCl for Db experiments are higher than or equal to 4 M HCl on the assumption that the extraction sequence is Nb $\geq$ Db as reported in chemical experiments[56,57] and theoretical calculation.[107]

2. 5 Conclusion

Solid-liquid extraction behaviors of Zr, Hf, and Th (as homologues of Rf) were investigated in the Aliquat 336/HCl system by manual batch method. The Q_d values were determined as a function of the shaking time. It was found that the extraction reaction of these elements reached equilibrium with shaking time for 10 s and suitable Aliquat 336 resin concentration was found at least higher than 28 wt%. The K_d values of these elements in equilibria on the HCl concentration were investigated. The abundances of anionic chloride complexes of Zr and Hf increase with an increase in the concentration of HCl, although the Th does not form anionic species. In this work, comparison data for Rf was obtained. Based on these results, ideal first Rf experimental condition were determined to be 7–9 M HCl for solid-liquid extraction using 28 wt% Aliquat 336 resin.

The distribution behaviors of Nb, Ta, and Pa were investigated in cation-exchange adsorption and solid-liquid extraction by Aliquat 336 from from 0.080–11.0 M HCl. The Q_d values were determined as a function of the shaking time. It was found that the cation-exchange reactions of these elements reached equilibrium within 10 s. Those in Aliquat 336 extraction, however, reached equilibrium only for Nb and Pa after 10 s of shaking, while required 2–3 h for Ta. This difference suggests that the formation reactions of the anionic complex and/or distribution of the ion-pair complex of Ta are slower than those of Nb and Pa. In addition, the dependency of K_d on HCl concentration at equilibrium was investigated for cation-exchange adsorption and Aliquat 336 extractions. Overall, the dominant Nb species were neutral and anionic for HCl concentrations of 0.1–4 M and 4–11 M HCl, respectively. In addition, the dominant Ta species varied between cationic ones in 0.08–0.5 M HCl, neutral in 0.5–5 M HCl, and anionic in 5–11 M HCl. Finally, the dominant Pa species varied between cationic ones in 0.1–2 M HCl, neutral in 2–3 M HCl, and anionic in 3–11 M HCl. Additionally, the dependency of K_d of the Aliquat 336 concentration suggested net charges of -1 for Nb in 6–10 M HCl, Ta in 6 M HCl, and Pa in 6 M HCl. The K_d values obtained for cation-exchange adsorption were in the order as Pa > Ta > Nb at equilibrium. Meanwhile, the K_d values for Aliquat 336 extraction were in the order as Pa > Ta > Nb at equilibrium. It assumed that the different extraction behaviors of Nb and Ta were attributed to their different chemical conformations.

Based on these results, ideal experimental conditions for Db was determined to be 0.080–11.0 M HCl in the cation-exchange adsorption, 4–11 M HCl for solid-liquid extraction using Aliquat 336 resin. Overall, the extraction kinetics of Db is particularly interesting, because those of homologues: Nb, Ta, and Pa are different from each other in Aliquat 336/HCl system.

Chapter 3. Development of an Automated Batch-Type Solid-Liquid Extraction Apparatus and Its Application to On-line Experiment of Zr and Hf

3.1 Introduction

We performed solid-liquid extraction of Zr and Hf with TIOA resin from HCl using AMBER. However, the chemical reaction container of AMBER had two problems; liquid spill and reflux.[62] To resolve these problems, in this work, a new container was developed. In addition, in a TIOA/HCl system, the Zr and Hf species adsorbed on the resin were not stripped by washing the resin with 4 M HCl which have been widely used for the stripping of these elements on the anion-exchange resin.[40,43–45] Therefore, 6 M HNO_3/0.01 M HF was used for stripping.[62] In this case, the K_d values were gradually decreased at repetitive experiments, and thus the TIOA resin was able to be reused only about five times, which is large problem for Rf experiment. The TIOA resin was not so suitable, because the same resin is needed to reuse in the repetitive experiments using AMBER. Extraction system was re-examined; the Aliquat 336/HCl system was tested in Section 2.1. Herein, to resolve two problems, a new chemical reaction container was developed, and AMBER was completed. By using the AMBER, back extraction of Zr and Hf from Aliquat 336 resin by 4 M HCl was studied. Subsequently, the solid-liquid extraction of Zr and Hf was carried out without renewing the resin to investigate number of repetitive experiment. Then, the on-line extraction experiment was performed in the Aliquat 336/HCl system using AMBER with ^{89g,m}Zr and ^{173}Hf produced by the accelerator at RCNP.

3.2 Experimental

3.2.1 Development of Extraction Apparatus

A new chemical reaction container was developed based on a previous three-layer structure container.[62] Outline and pictures of the new chemical reaction container were shown in Figures 3-1(a)–(c). Chemical reaction containers, in which the solution sample and resin were mixed to extract the reaction products to the resin phase, were made of polychlorotetrafluoroethylene (PCTFE), and the volume to contain was about 0.6 mL. The major change of the container was an application of the o-ring and hole size of the bottom of the container which was changed from Φ2 to Φ4 to decrease inner pressure. The top of lower parts was changed from flat to 1 cm of hole to set a PTFE filter.

An internal diameter of the PTFE tubes of the downstream of the container was changed from 0.17 to 1.0 mm to enable fast phase separation at low pressure of compressed air. So far, to prevent from liquid spill, inlet (top) of the container was released during shaking, which caused the reflux of the solution from inlet. By applying near container with an o-ring, liquid spill was prevented. Therefore, inlet was closed daring shaking and reflux was also prevented.

The setup of the AMBER for repetitive experiments was shown in Figure 3-2. The two-way switching valves and three-way slider-type switching valves for the passage of solution were made of PCTFE and were moved by air cylinders. These cylinders were moved by on/off operation of DC power (24 V). A compactDAQ device and LabVIEW software from National Instruments were used for these operations, and all the operations were controlled with fixed time intervals in on-line extraction experiments. The 2 two-way switching valves and the Automated Slider-type dissolution equipment (ASO) were connected by PTFE tubes. The ASO and three-way slider-type switching valves were connected by PTFE tubes (0.17 mm i.d.; 30 cm long). The three-way slider-type switching valves and chemical reaction containers were connected with PTFE tubes (0.17 mm i.d.; 10.5 cm long). At the bottom of the container, a PTFE filter with a pore size of 10 μm was set to push out only the solution with 10 s of compressed air after the extraction.

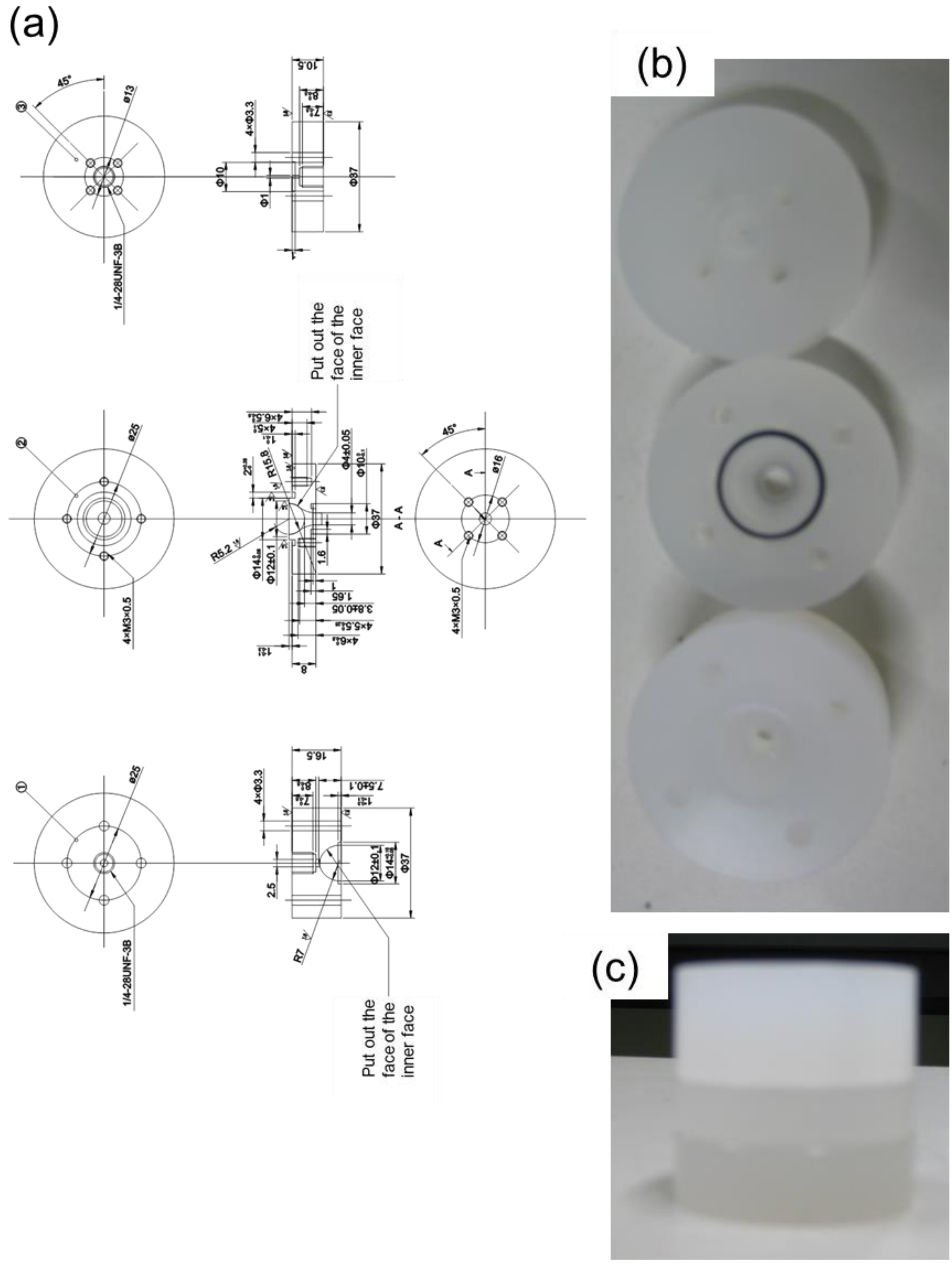


Figure 3-1. (a) Structural layout of chemical reaction container. (b) and (c) pictures of chemical reaction container.

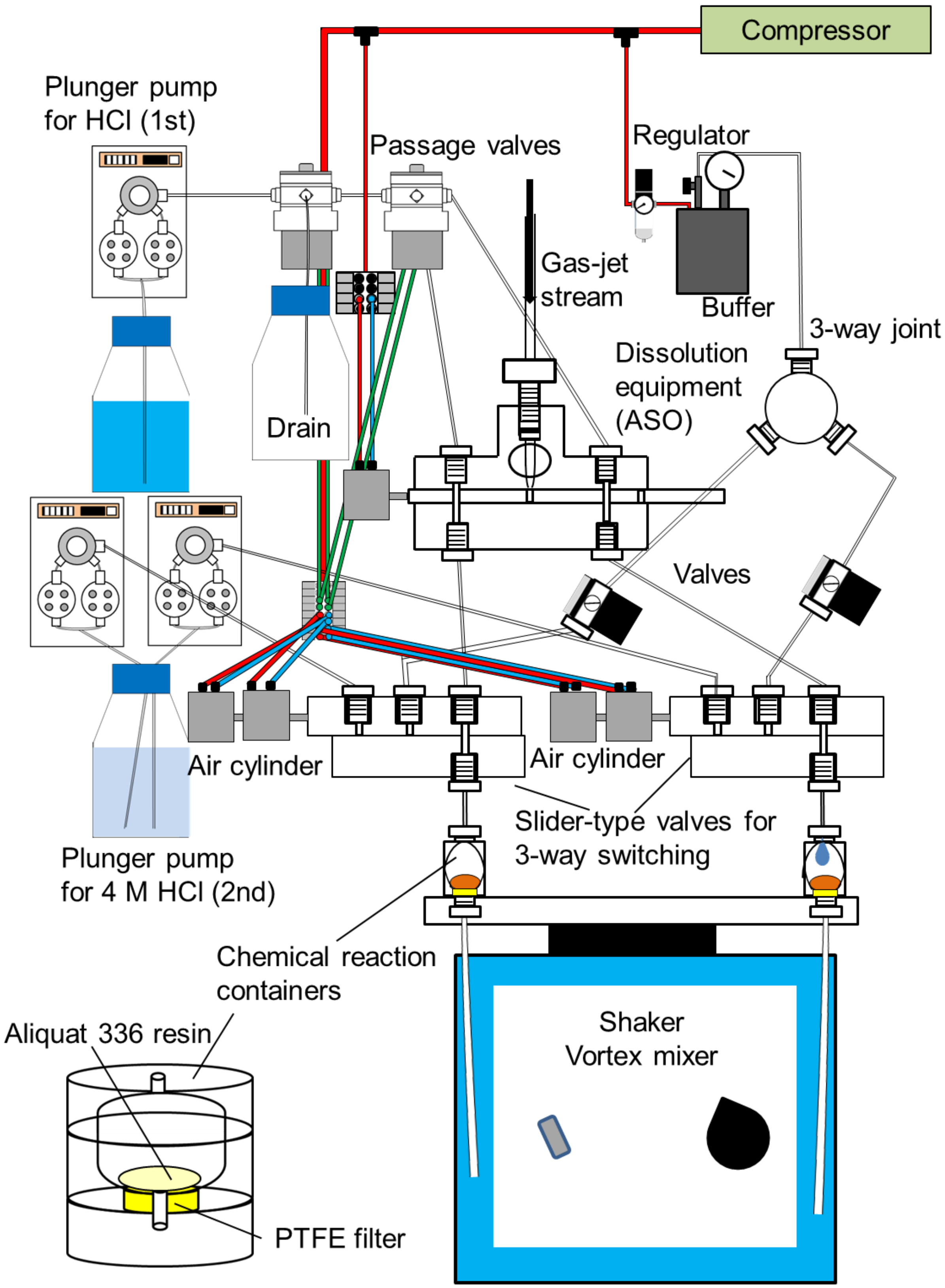


Figure 3-2. Schematic diagram of the AMBER. Compressor supplies compressed air through a buffer tank to air cylinders and chemical reaction containers. Eluate from the ASO goes through a slider-type valve into a chemical reaction container.

3.2.2 Off-Line Extraction Experiment

In the off-line experiment using AMBER, the solid-liquid extraction of Zr and Hf was performed as following procedure. The 1.7–4.5 mg of the 28–48 wt% Aliquat 336 resins and 0.25 mL of 10 M HCl containing the ^{88}Zr and ^{175}Hf tracer solutions were manually put in a chemical reaction container and shaken at ~20 ºC for 10 s using the shaker. Subsequently, only the solution phase was pushed out of the container by the compressed air at 0.5 MPa and was collected in a PP tube. The Zr and Hf species adsorbed on the resin were stripped by washing the resin 3–9 times for 3 or 5 s with ~0.3 mL for 4 M HCl. Subsequently, only the solution phases were pushed out of the container and were collected in the PP tubes. All the solution samples were subjected to γ-ray measurement using a Ge detector. For indirect measurement of the radioactivity on the resin by the method described in the off-line extraction experiment (Subsection. 2.2.3), a control extraction experiment without resin was performed to determine the radioactivities of the control solution. In the solid-liquid extraction experiment without renewing the resin, the ^{88}Zr and ^{175}Hf tracers were added in only 1, 10, 20, 30, 40, 50, 61, 77, 86, and 102 th extraction, and the total number of cycle experiment was 102 times.

The back extraction yield (Y_{bk}) was determined from the following equation:

$$Y_{\mathrm{bk}m} = \frac{\sum_{l=1}^{m} A_{\mathrm{b}l}}{\sum_{l=1}^{n} A_{\mathrm{b}l}} \times 100 \qquad (3\text{-}1)$$

,

where A_{b} is radioactivity in the stripped solution, and m is the number of back extraction (m = 1–n), and n is the total number of back extraction. Completely stripped Zr and Hf species from Aliquat 336 resin corresponds to Y_{bk} = 100%.

The K_{d} values were obtained by equation 2-2 in Subsection 2.1.2. In this work, the method to evaluate the K_{d} values was defined using the control solution as the control method and that using the radioactivity in the stripping solution as the 2-solution method (2-soln. method). In the control method, the A_{r} was obtained by as $A_{\mathrm{c}} - A_{\mathrm{s}}$. In the 2-soln. method, the A_{r} was be determined from the radioactivities in the stripping solutions.[61]

3.2.3 On-Line Extraction Experiment

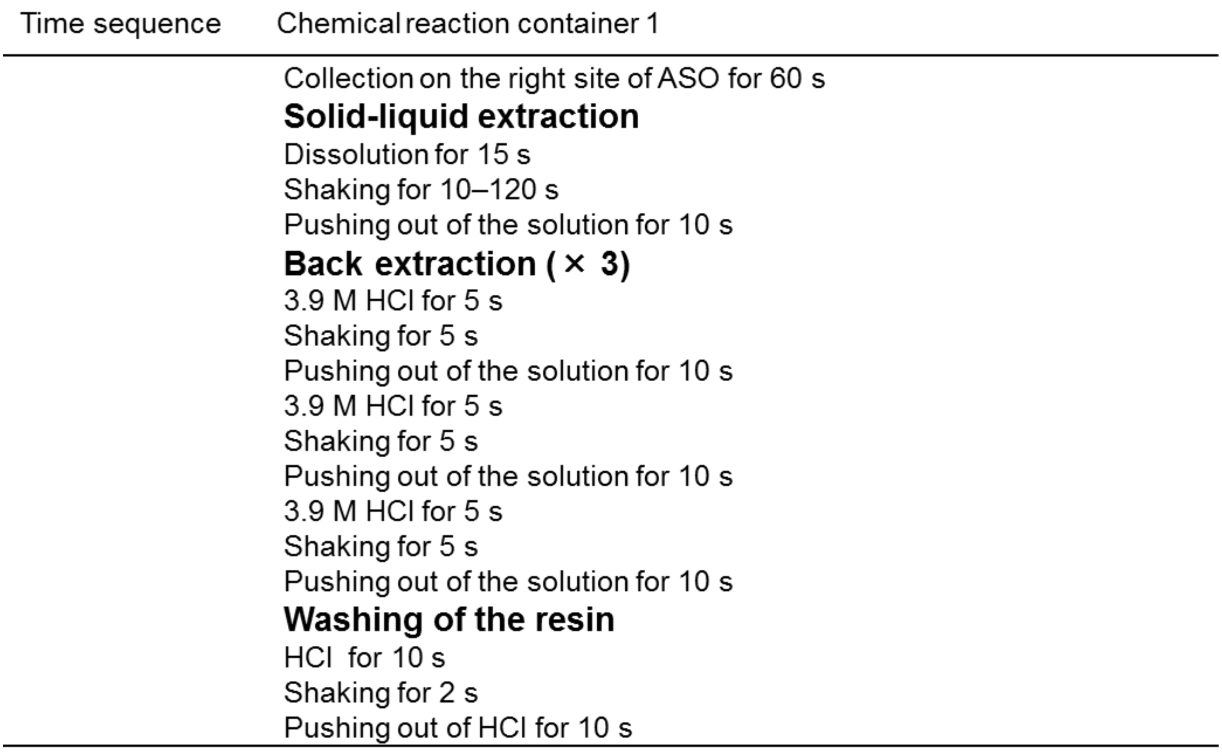
The on-line experiment using AMBER was performed with relatively short-lived nuclides ^{89g,m}Zr ($T_{1/2}$ = 3.27 d, 4.18 min) and ^{173}Hf ($T_{1/2}$ = 23.6 h) produced in the ^{nat}Zr(α,xn)^{89g,m}Zr and ^{nat}Yb(α,xn)^{173}Hf reactions, respectively, using the AVF cyclotron at RCNP. The nuclides produced in the bombardment of 1 sheet of ^{nat}Sr and 4 sheet of ^{nat}Yb on the 3 μm of Al backing foil with ^{4}He (α) projectile with energy of 40 MeV. The beam current was ~1.3 μA. The nuclear reaction products, recoiling out of the target, were caught by KCl aerosols in He gas at ~135 kPa. The products were transported by the He gas with the flow rate of 2.5 L/min to a chemistry laboratory (see Figure 1-4).

The time sequence in one shot of control extraction experiment and solid-liquid extraction experiments are shown in Figures 3-3 and 3-4, respectively; the corresponding sequence of repetitive experiments of the control extraction and solid-liquid extraction experiments are shown in Figures 3-5 and 3-6, respectively. The transported products were deposited on a collection site on a slider in ASO for 60 (10 and 120 s of shaking experiments), 133 (10 s of shaking experiment), or 153 s (30 s of shaking experiment). Subsequently, the deposited sample was dissolved in average 0.23 mL of 8.2, 9.2, 10.3, and 11.2 M HCl. The solution sample entered the chemical reaction container containing 1.7–3.8 mg of the 28 wt% Aliquat 336 resin. After shaking at 27 ± 1 ºC for 10, 30, and 120 s, only the solution phase was pushed out of the container by the compressed air at approximately 0.15 MPa for 10 s and was collected in a PP tube. The sample was subjected to the γ-ray (^{89g}Zr: E_γ = 909.0 keV, ^{89m}Zr: E_γ = 587.8 keV, ^{173}Hf: E_γ = 297.0 keV) measurements with the Ge detector. The Zr and Hf species adsorbed on the resin were stripped by washing the resin 3 times with ~0.29 mL of 3.9 M HCl and each solution was collected in the PP tubes. The γ-ray activities of all the stripped solutions were measured. Then, the resin was conditioned with HCl for the next extraction. Control experiments without the Aliquat 336 resin were separately performed. The Q_d values were determined by both control and 2-soln. methods from equation 2-2.

To examine the time required to equilibrium in the extraction, the time dependences of the Q_d values were investigated in the range 10–120 s in 9.2 and 11.2 M HCl. In addition, the K_d values of Zr and Hf were determined in 8.2–11.2 M HCl.

Time sequence	Chemical reaction container 1
	Collection on the right site of ASO for 60 s
	Control extraction
	Dissolution for 15 s
	Shaking for 10–120 s
	Pushing out of the solution for 10 s
	3.9 M HCl for 5 s
	Washing of the container
	HCl for 10 s
	Shaking for 2 s
	Pushing out of HCl for 10 s

Figure 3-3. The time sequence of one shot of control extraction experiment.



Time sequence	Chemical reaction container 1
	Collection on the right site of ASO for 60 s
	Solid-liquid extraction
	Dissolution for 15 s
	Shaking for 10–120 s
	Pushing out of the solution for 10 s
	Back extraction (× 3)
	3.9 M HCl for 5 s
	Shaking for 5 s
	Pushing out of the solution for 10 s
	3.9 M HCl for 5 s
	Shaking for 5 s
	Pushing out of the solution for 10 s
	3.9 M HCl for 5 s
	Shaking for 5 s
	Pushing out of the solution for 10 s
	Washing of the resin
	HCl for 10 s
	Shaking for 2 s
	Pushing out of HCl for 10 s

Figure 3-4. The time sequence of one shot of solid-liquid extraction experiment.

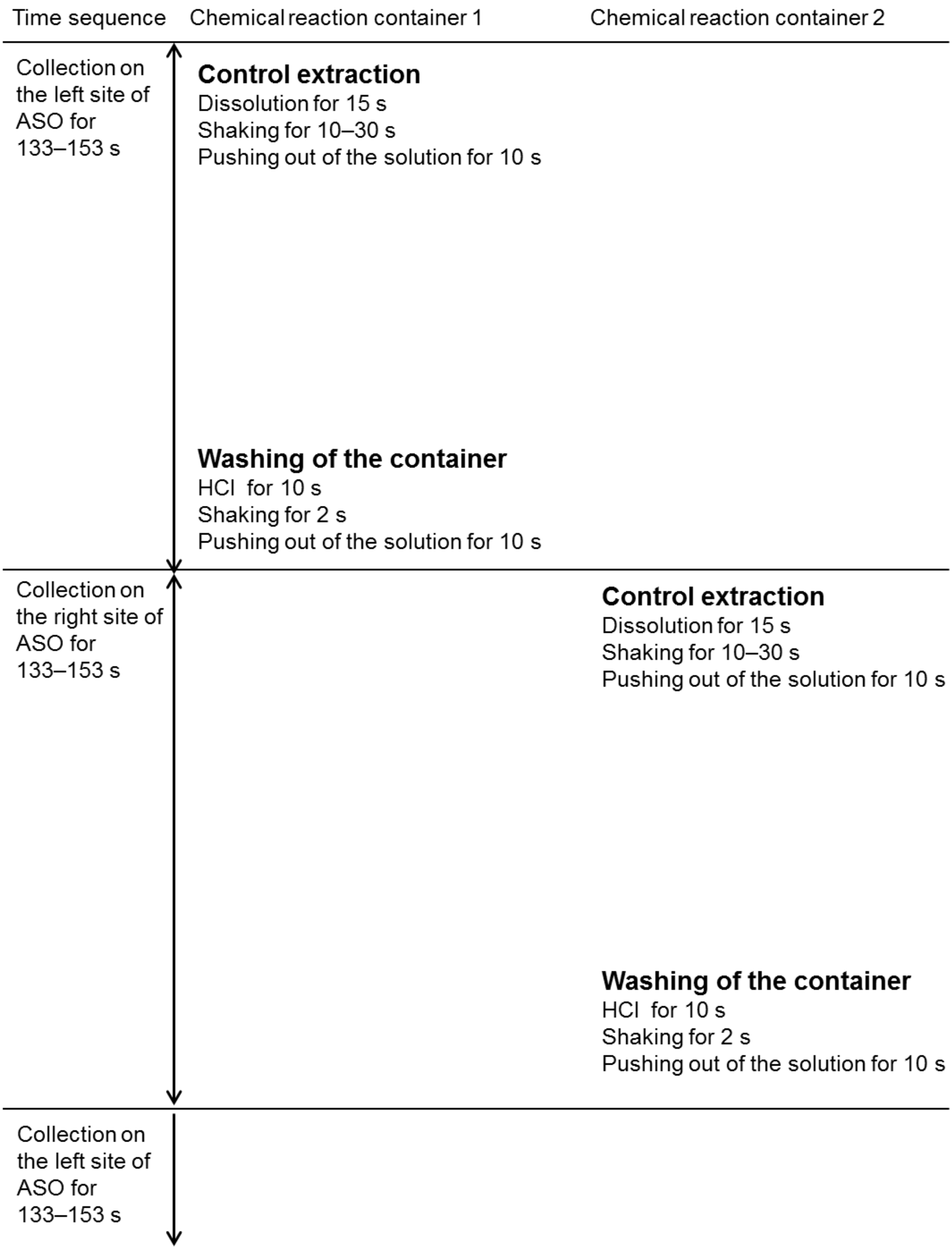


Figure 3-5. The time sequence of repetitive experiment of control extraction experiment.

Time sequence	Chemical reaction container 1	Chemical reaction container 2
Collection on the left site of ASO for 133–153 s	**Solid-liquid extraction** Dissolution for 15 s Shaking for 10–30 s Pushing out of the solution for 10 s **Back extraction (× 3)** 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s **Washing of the resin** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s	
Collection on the right site of ASO for 133–153 s		**Solid-liquid extraction** Dissolution for 15 s Shaking for 10–30 s Pushing out of the solution for 10 s **Back extraction (× 3)** 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s **Washing of the resin** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s
Collection on the left site of ASO for 133–153 s		

Figure 3-6. The time sequence of repetitive experiment of solid-liquid extraction experiment.

3.3 Results and Discussion

3.3.1 Off-Line Extraction Experiment

The liquid spill at the bottom of the container and the liquid reflux at the top of the container were solved by applying a new chemical container and changing the operation as mentioned are above. The dependence of the Y_{bk} values of Zr and Hf on the back extraction number are shown in Figure 3-7: for the extraction with 28 wt% Aliquat 336 resin with 5-s shaking in (a) and 3-s shaking in (b). The corresponding data for the 35 and 48 wt% Aliquat 336 resins with 5-s shaking are shown in (c) and (d), respectively. The Zr and Hf species adsorbed on the Aliquat 336 resins were able to be stripped by 4 M HCl, which was different from the TIOA case. From 28 wt% Aliquat 336 resin, 3 times back extractions were required for larger than 99% stripping with 5-s shaking and 5 times were required with 3-s shaking, suggesting that the back extraction reaction dose not reach equilibrium with 3 s. However, whether the back extraction reaction is reached equilibrium with 5 s or not is not known. For 5-s shaking, the necessary back extraction numbers are 5 times from 35 wt% Aliquat 336 resin and 6 times from 48 wt% Aliquat 336 resin. In the single back extraction, the back extraction yields of Zr and Hf decreased as Aliquat 336 concentration increased to 48 wt%. Therefore, TIOA concentration is considered to be too high to strip adsorbed Zr and Hf species by 4 M HCl. Although adsorbed species might be able to be stripped by 4 M HCl from low concentration (< 31 wt%) of TIOA resins, the extraction equilibrium of Zr and Hf need to ~20 min with 18 and 25 wt% TIOA resins.[61] To use the TIOA resins, re-examine stripping agent or to renew the resin each five times are needed. The back extraction yields of Zr were higher than those of Hf, indicating that anionic chloride complexes of Zr is likely to form dechlorinated cationic and/or neutral species compared to those of Hf. To perform rapid and repetitive experiments, small number of back extraction is expected. From these results, three times back extraction with 5-s shaking using 28 wt% Aliquat 336 resin is the most Rf suitable condition for Rf experiment, and should be applied to the first Rf experiment.

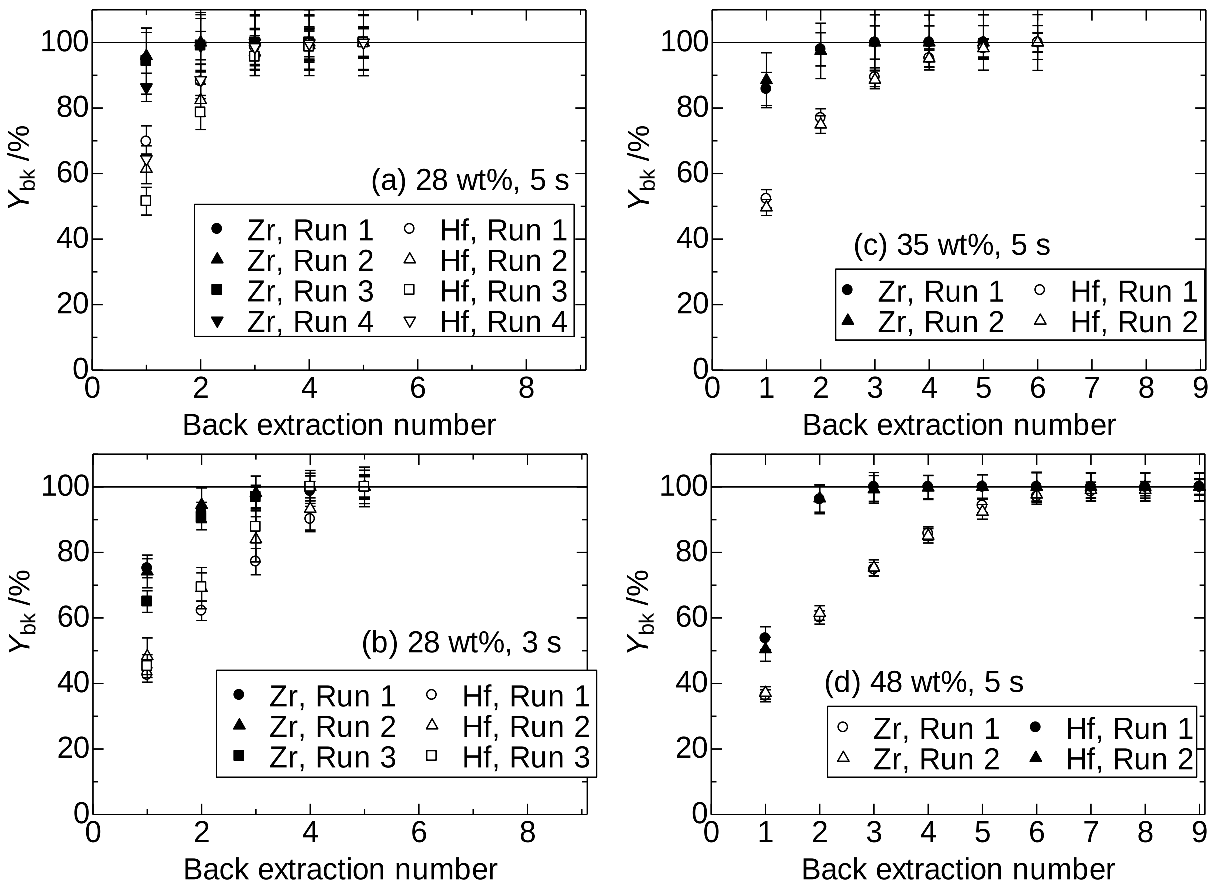


Figure 3-7. The Y_{bk} of Zr and Hf as a function of number of back extraction from (a), (b) 28 wt%, (c) 35 wt%, and (d) 48 wt% (d) Aliquat 336 resins with 4 M HCl for (a), (b), and (c) 5-s and (b) 3-s shaking.

The K_d values of Zr and Hf as a function of the number of solid-liquid extraction cycle without renewing the resin are shown in Figure 3-8. Values remain roughly constant for all experiments, indicating that constant K_d values can be obtained in the repetitive 102 times extraction without renewing the resin. The same resin was found to be used in at least 102 times. From this result, it was found that the 28 wt% Aliquat 336 resin is more suitable for Rf experiment than the TIOA resin. In the following on-line experiments, the 28 wt% Aliquat 336 resin was used. The K_d values evaluated by the control method were consistent with those found by the 2-soln. method, suggesting that the K_d values in the solid-liquid extraction in the present reaction system can be obtained by both the methods using AMBER.

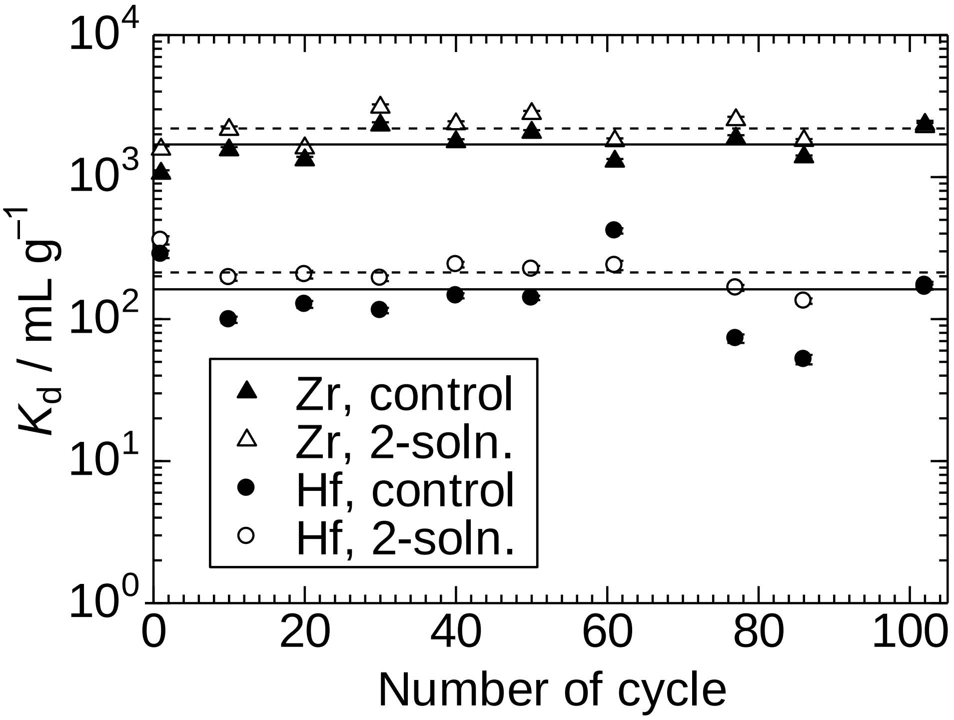


Figure 3-8. The K_d values of Zr and Hf as a function of number of cycle extraction from 10 M HCl with 28 wt% Aliquat 336 resin with shaking for 10 s. Solid lines are average of the K_d values by control method and broken lines are average of the K_d values by 2-soln. method.

3.3.2 On-Line Extraction Experiment

The radioactivities of the transported ^{89g,m}Zr and ^{173}Hf nuclides normalized by the beam current were almost constant during the present 1-day experiment. The chemical yield of ^{89g,m}Zr and ^{173}Hf were the same to be approximately 55%. The dependences of the Q_d values of Zr and Hf on the shaking time in the extraction with 28 wt% Aliquat 336 resin are shown in Figures 3-9(a) and (b), respectively. The Q_d values of Zr and Hf were almost constant from 10–120 s for all HCl concentrations, suggesting that an equilibrium was established within 10 s same as that in the off-line experiment. In the on-line experiment, contact time was shorter than that of off-line experiment, because separation of the solution and resin phases took several minutes in the off-line experiment. The Q_d values evaluated by the 2-soln. method were consistent with those found by the control method. By this method, separation between the solution and resin phases was accomplished within 10 s, while it usually takes longer than one minute for phase separation using centrifugation and pipetting in the ordinary manual batch experiment.

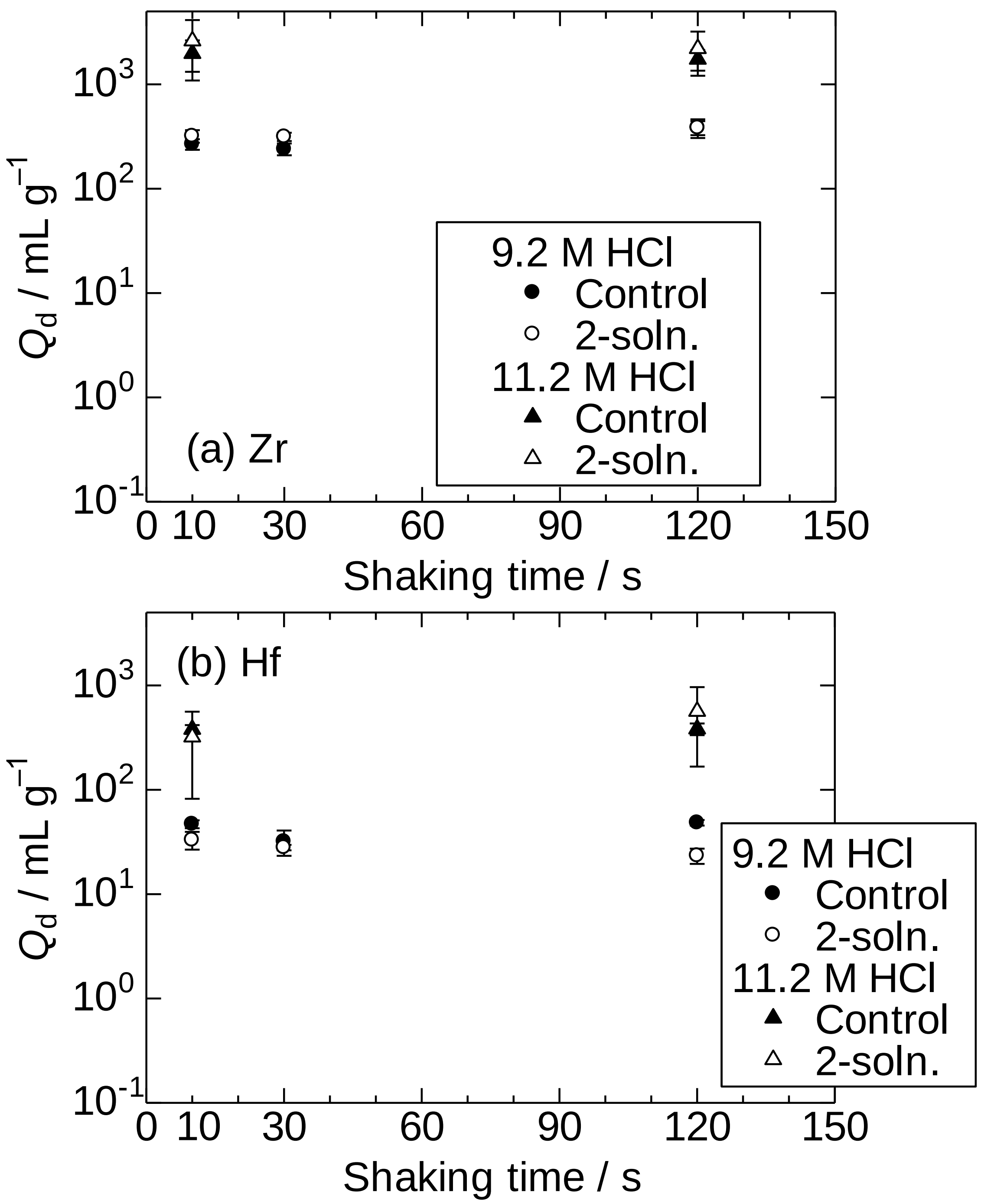


Figure 3-9. The Q_d values of (a) Zr and (b) Hf for different shaking times in 9.2 and 11.2 M HCl with 28 wt% Aliquat 336 resin.

The dependence of the K_d values of Zr and Hf on the HCl concentration in the extraction with 28 wt% Aliquat 336 resin is shown in Figure 3-10, together with the equilibrated data in the off-line experiment (Subsection 2.1.2). The K_d values of Zr and Hf in the on-line experiment (control and 2-soln. methods) were in good agreement with those in the off-line experiment except the data in 8.2 M HCl. In 8.2 M HCl, the K_d value of Hf in the on-line experiment is higher than that in equilibrium possibly because of the influence of physical adsorption on the resin or chemical reaction container etc. From this study, the K_d values can be obtained by both the control and 2-soln. methods in wide range of HCl concentration. It was found that chloride complex formations of Zr and Hf could be investigated using rapid solid-liquid extraction apparatus in the on-line experiment.

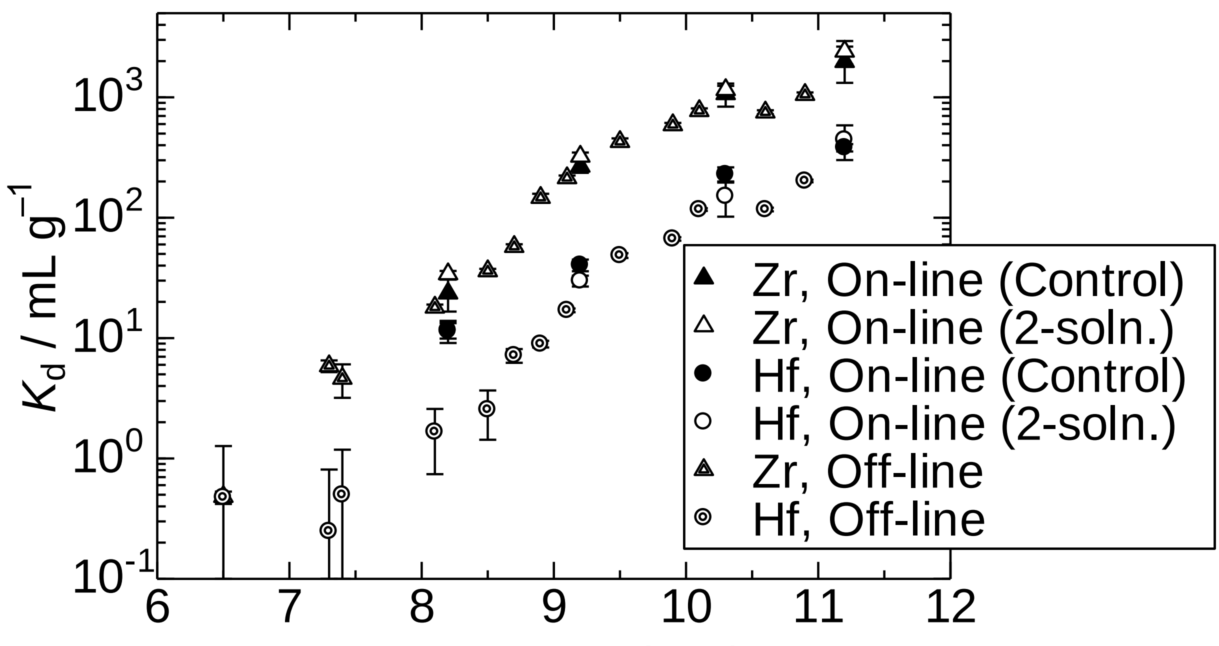


Figure 3-10. The K_d values of Zr and Hf as a function of HCl concentration with 28 wt% Aliquat 336 resin.

3.3.2 Solid-Liquid Extraction Experiment for Rf Using Automated Batch-Type Solid-Liquid Extraction Apparatus

By using AMBER, the solid-liquid extraction procedures can be accomplished rapidly and automatically, and the K_d values can be obtained by both the control and 2-soln. methods. When the K_d value is evaluated by the 2-soln. method, the stripping solution need to be subjected to radiation measurements. Even with shaking for 10 s, it took 95 s until pushing out of stripping solution thrice from the start of the dissolution of the products transported by the gas-jet system (extraction: 15-s dissolution, 10-s mixing, and 10-s elution; washing (thrice): 5-s injection of washing solution, 5-s mixing, and 10-s elution). In addition, the stripping solution must be evaporated to detect α particles from the sample in the extraction of Rf. Consequently, the 2-soln. method has low applicability for Rf experiments considering the half-life of ^{261}Rf (68 s).[81] On the other hand, by the control method, the stripping of the resin is not necessary, and it took only 35 s until pushing out of all the eluent or control solution (in the case of control experiment) with a shaking time of 10 s. Although an additional ~40 s is needed for the evaporation of about 0.25 mL of eluent in the Rf experiment, sufficiently fast sample preparation about 80 s inducing 35 s for extraction with 10-s shaking and 40-s evaporation could be accomplished by the control method using AMBER.

The K_d values were influenced by physical adsorption when the K_d values were especially small. Therefore, the condition of the small K_d values should be excluded. From such point of view, suitable HCl concentration 7–8 M and 8–9 M for first Rf experiment is in the solid-liquid extraction by 28 wt% Aliquat 336 resin on the assumption that the extraction sequence is Rf > Zr > Hf as reported in anion-exchange experiment using hot HCl (80 ºC)[10,40] and Zr > Hf > Rf (4–8 M HCl) as reported in theoretical calculation, respectively.[49] Based on these points,[10,40,49] ideal first time dependence of Rf experimental condition for would be ~8 M HCl.

3.4 Conclusion

A new chemical reaction container of AMBER was developed and also changed working of AMBER. By these improvements, the liquid spill and reflux at chemical reaction container did not happen. Adsorbed Zr and Hf species on the Aliquat 336 resin were able to be stripped by 4 M HCl. The required back extraction number increased with an increase of the Aliquat 336 concentration. With 28 wt% Aliquat 336 resin, the back extraction yields of Zr and Hf with 5-s shaking were higher than those with 3-s shaking. The 28 wt% Aliquat 336 resin was able to used higher than 100 times in the solid-liquid extraction without renewing the resin. From these results, 28 wt% Aliquat 336 resin was suitable for Rf experiments. By using AMBER, on-line solid-liquid extraction experiment by 28 wt% Aliquat 336 resin from HCl for ^{89g,m}Zr and ^{173}Hf nuclides produced by the accelerator at RCNP was successfully performed. The Q_d values of Zr and Hf obtained with shaking time of 10–120 s were approximately constant, suggesting that the extraction reaction reach equilibrium within 10 s. The K_d values in the on-line experiment were consistent with those in the off-line batch experiment except for Hf in 8.2 M HCl. To carry out solid-liquid extraction experiment of Rf by the control method was decided, because the K_d values of Zr and Hf by the control method were good agreement with those by the 2-soln. method, and the experiments was rapidly accomplished. Based on these results, ideal first time dependence of Rf experimental condition for to be approximately 8 M HCl for solid-liquid extraction using 28 wt% Aliquat 336 resin were determined.

Chapter 4. Solid-Liquid Extraction of Rf with Aliquat 336 from HCl

4.1 Introduction

To study the extraction behavior of Rf in equilibrium, solid-liquid extraction of Zr, Hf, and Th in the Aliquat 336/HCl system was performed (section 2.1), and the batch-type solid-liquid extraction apparatus, AMBER, was developed (Chapter 3). Herein, the solid-liquid extraction experiment of Rf from 7.9 and 9.0 M HCl by the 28 wt% Aliquat 336 resin were performed using AMBER with ^{261}Rf produced by the high intensity accelerator at RIKEN, and the time dependency of the Q_d values were investigated, which is the first observation of equilibrium for transactinide elements.

4.2 Experimental

The on-line experiment using AMBER was performed with ^{261}Rf ($T_{1/2}$ = 68 s)[81] and ^{169}Hf ($T_{1/2}$ = 3.24 min) nuclides produced in the ^{248}Cm(^{18}O,5n)^{261}Rf and ^{nat}Gd(^{18}O,xn)^{169}Hf reactions, respectively using the K 70 AVF cyclotron at RIKEN. The nuclides produced in the bombardment of 685.2 μg/cm^2 of ^{248}Cm and 69.6 μg/cm^2 of ^{nat}Gd mixture on the 1.880 mg/cm^2 of Be backing foil with ^{18}O projectile with energy of 109 MeV. The beam current was ~0.8 particle-μA. The nuclear reaction products, recoiling out of the target, were caught by KCl aerosols in He gas at ~130 kPa. The products were transported by the He gas with the flow rate of 2.5 L/min to a chemistry laboratory (see Figure 1-4).

The schematic and photographs of solid-liquid extraction experimental setup (ASO, AMBER, and automated rapid α/SF detection system[60]) are shown in Figures 4-1(a)–(c). The time sequence of 10- and 30-s shaking control extraction experiments are shown in Figures 4-2 and 4-3, respectively; the corresponding sequence of 10-, 30-, and 60-s shaking of the solid-liquid extraction experiments are shown in Figures 4-4, 4-5, and 4-6, respectively. The transported products were deposited on a collection site on a slider of the ASO for 133 (10-s shaking experiment), 128 (30-s shaking experiment), and 143 s (60-s shaking experiment). Subsequently, the deposited sample was dissolved in average 0.25 mL of 7.9 and 9.0 M HCl for 15 s. The solution sample entered the chemical reaction container containing 1.11–1.62 mg of the 28 wt% Aliquat 336 resin. After shaking at 26–27 ºC for 10, 30, and 60 s, only the solution phase was pushed out of the container by the compressed air at 0.10–0.15 MPa for 10 s and was collected on a Ta disk (Figure 4-1(c)).

The solution sample on the Ta disk was evaporated to dryness with two hot He gas (1.3 L/min; 300 ºC and 0.7 L/min; 600 ºC) and a halogen heat lamp to prepare a sample for α-particle measurement. Subsequently, the Ta disk was transferred to a detection chamber equipped with a Si PIN photodiode detector, and the α-particle measurement was conducted.[60] The eight chambers were used. The efficiency and energy calibration were performed using ^{241}Am (E_α = 5.49 MeV) and ^{212}Bi (E_α = 6.07 MeV)–^{212}Po (E_α = 8.78 MeV). The efficiency and energy resolution of the sample and detector arrangement were ~34% and 35–62 keV full width at half maximum (FWHM) at the 5.49-MeV α peak of ^{241}Am, respectively. The α-particle measurement started ~85 s (10-s shaking), ~105 s (30-s shaking), and ~135 s (60-s shaking) later from the start of the dissolution of the products transported by the gas-jet system and were performed for ~786 s. After the α-particle measurement, the γ-ray activity of ^{169}Hf (E_γ = 492.9 keV) was monitored using the Ge detector to determine its K_d value and the chemical yield.

The Rf and Hf species adsorbed on the resin were stripped by washing the resin 3 times with about 0.3 mL of 3.9 M HCl with 5-s shaking. Subsequently, the resin was conditioned with ~0.16 mL of HCl with the shaking time of 2 s for the next extraction. All the stripped and conditioned solutions were discarded.

The Aliquat 336 resin was reused 18–66 times and then renewed. Control extraction experiments without the Aliquat 336 resin were also performed to evaluate the A_r. A total of 379 cycles of the procedures were conducted.

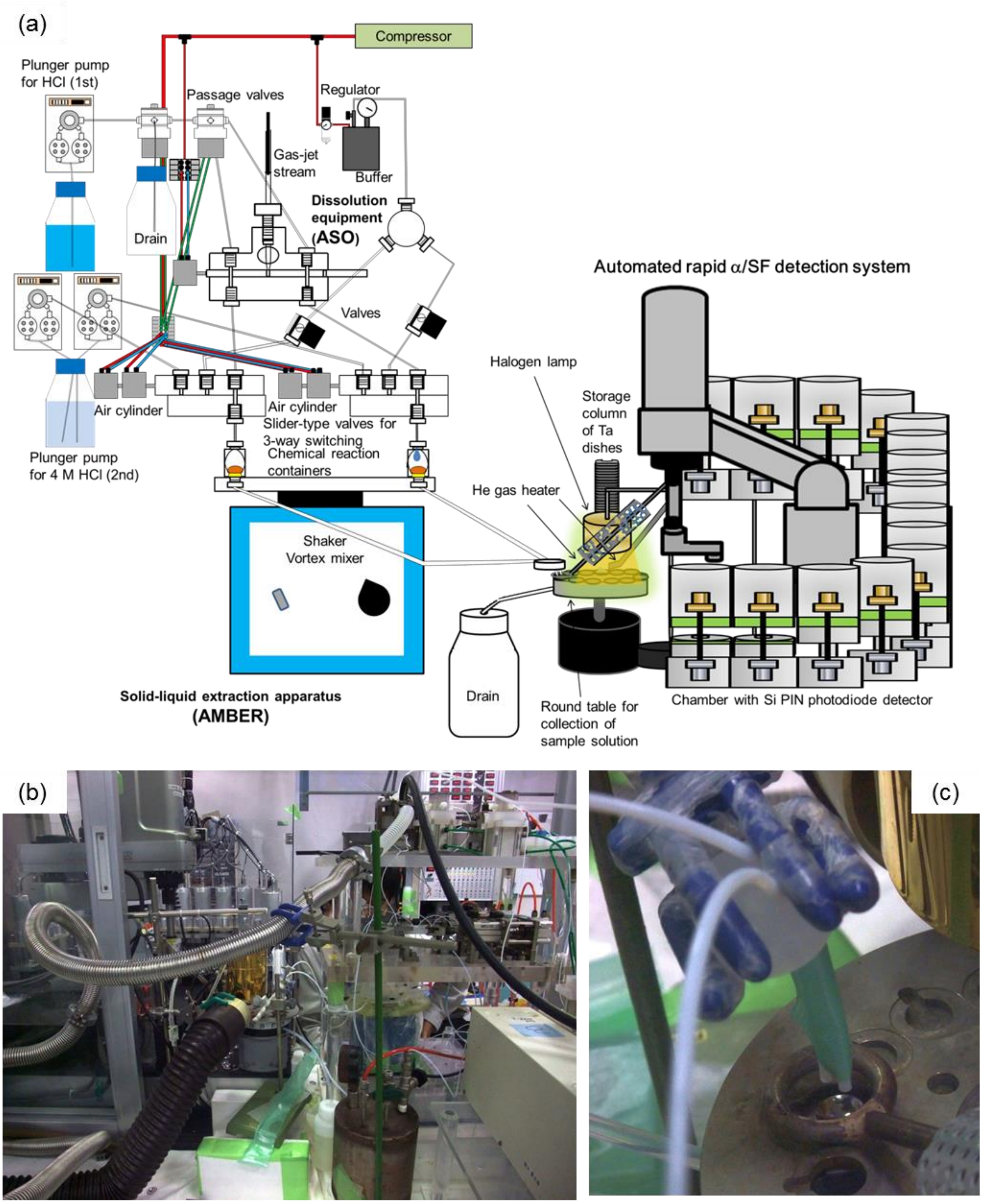
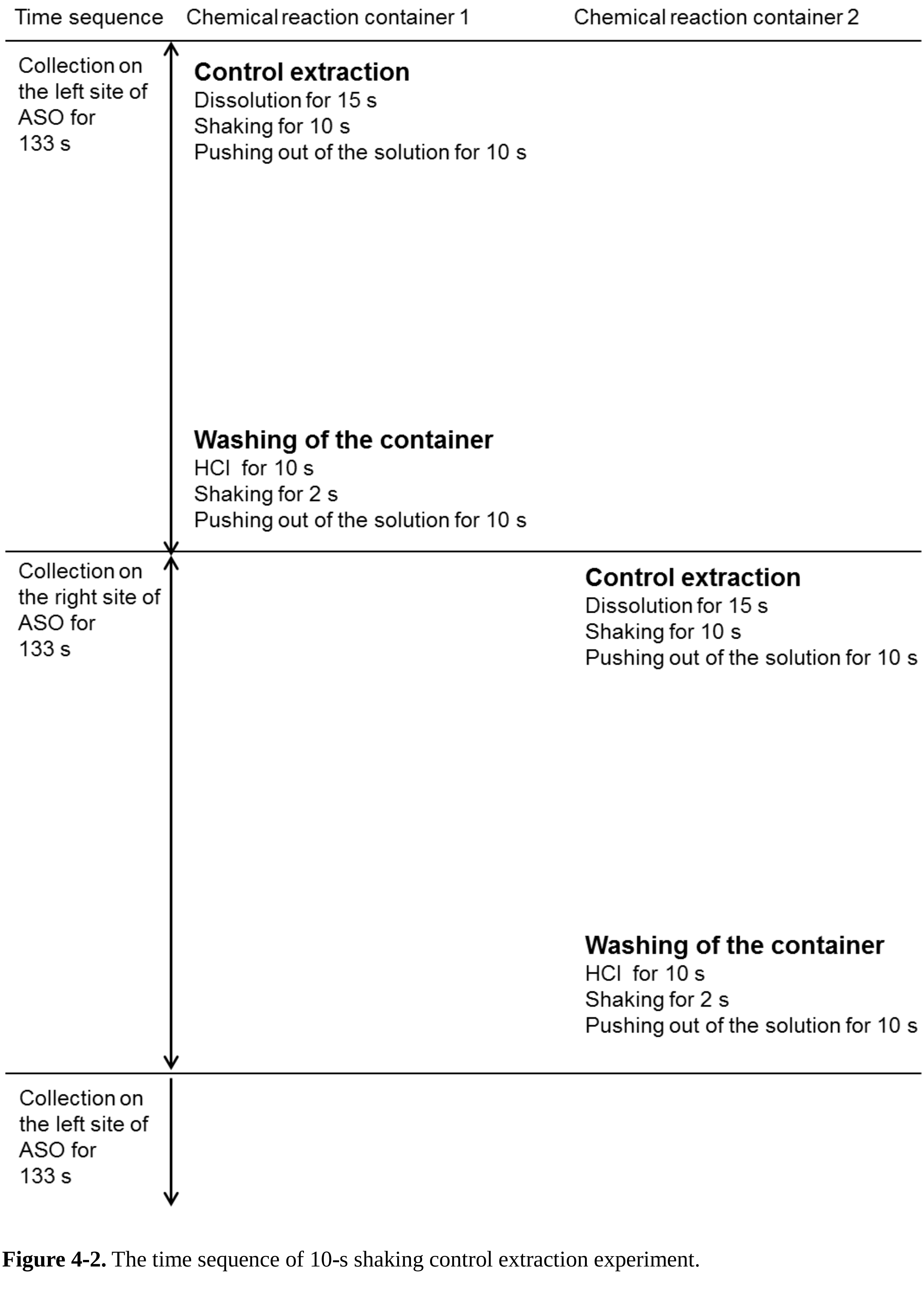


Figure 4-1. (a) Schematic drawing and (b) photograph of the experimental setup, and (c) photograph of the collection of the solution sample on a Ta disk.



Time sequence	Chemical reaction container 1	Chemical reaction container 2
Collection on the left site of ASO for 133 s	**Control extraction** Dissolution for 15 s Shaking for 10 s Pushing out of the solution for 10 s **Washing of the container** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s	
Collection on the right site of ASO for 133 s		**Control extraction** Dissolution for 15 s Shaking for 10 s Pushing out of the solution for 10 s **Washing of the container** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s
Collection on the left site of ASO for 133 s		

Figure 4-2. The time sequence of 10-s shaking control extraction experiment.

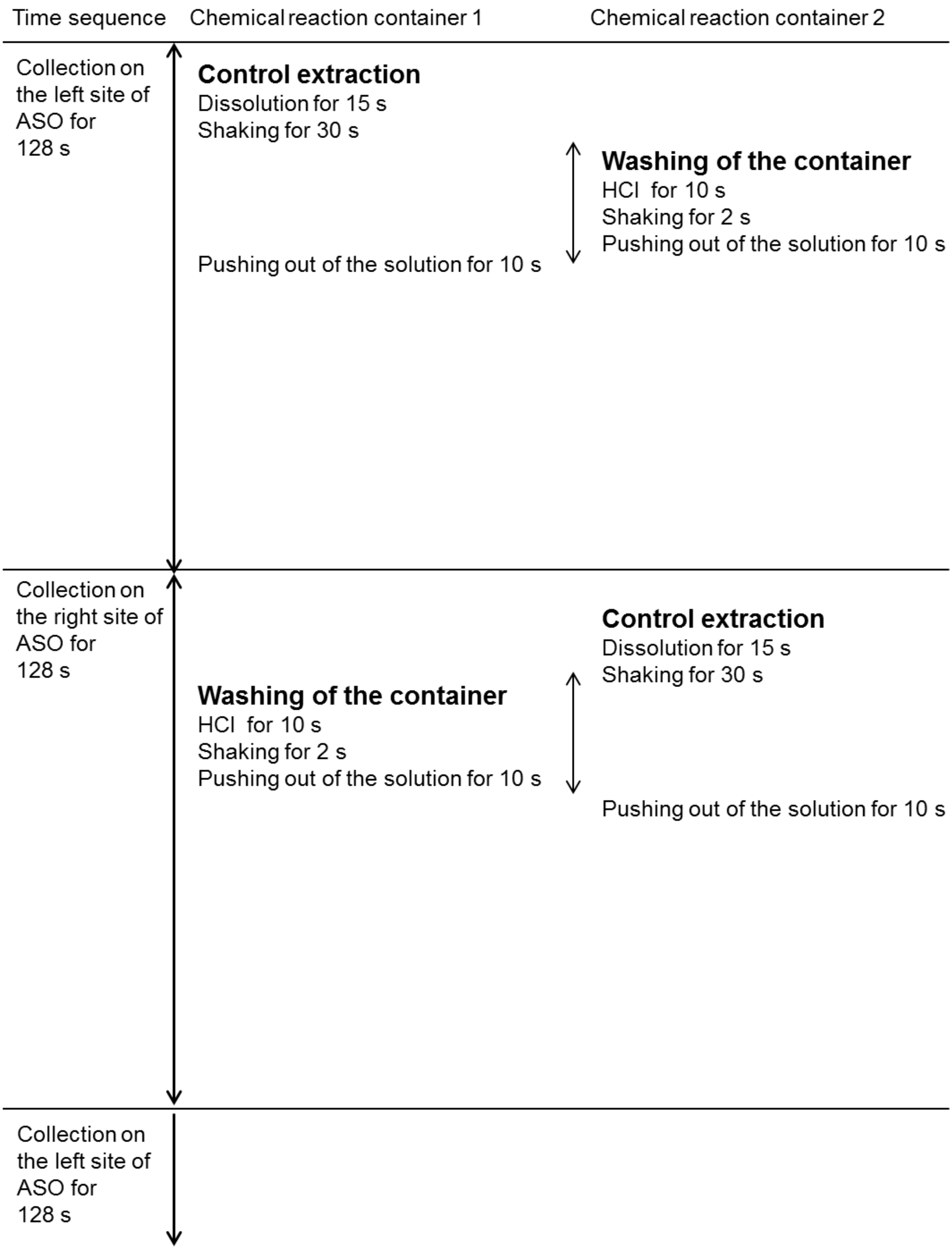
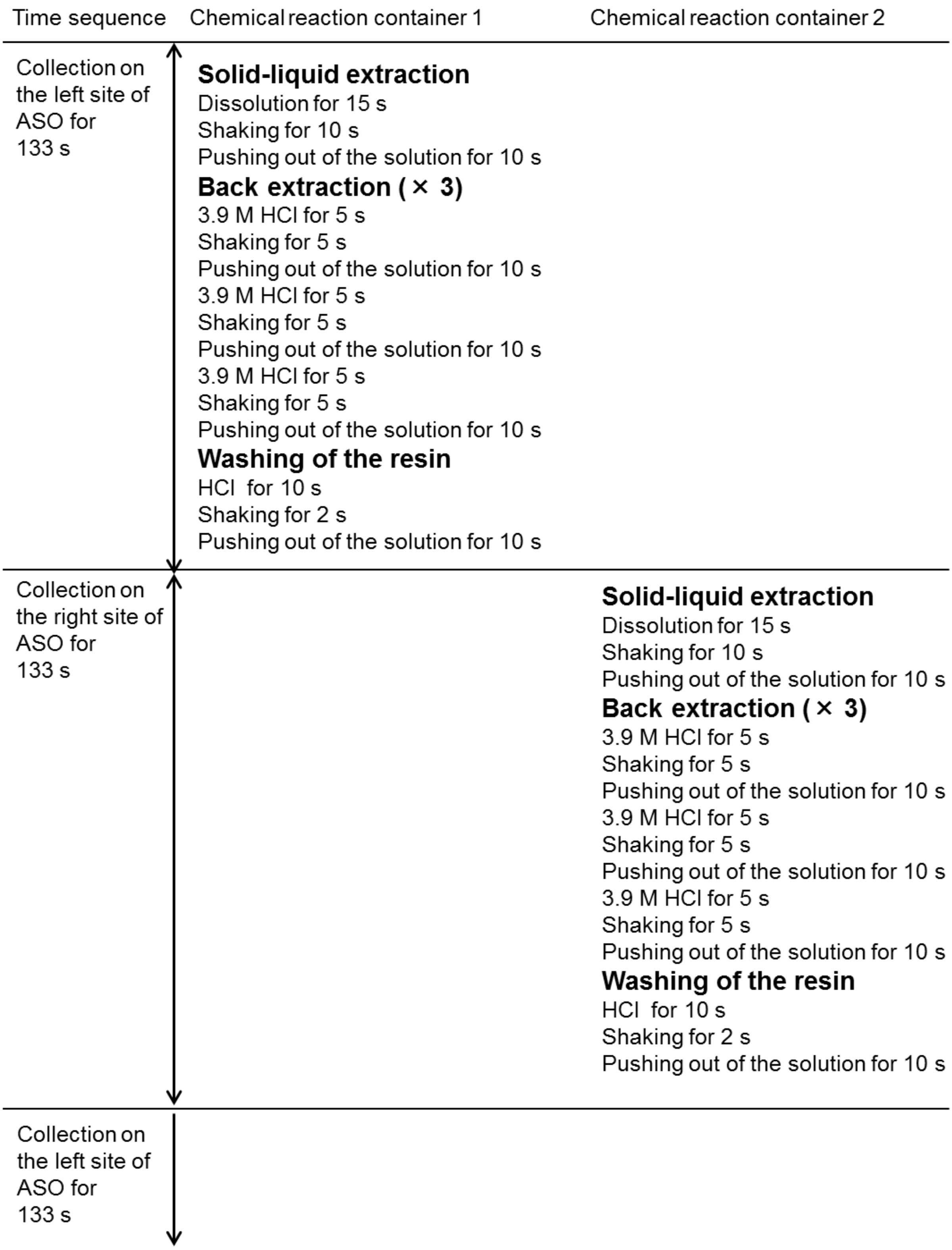
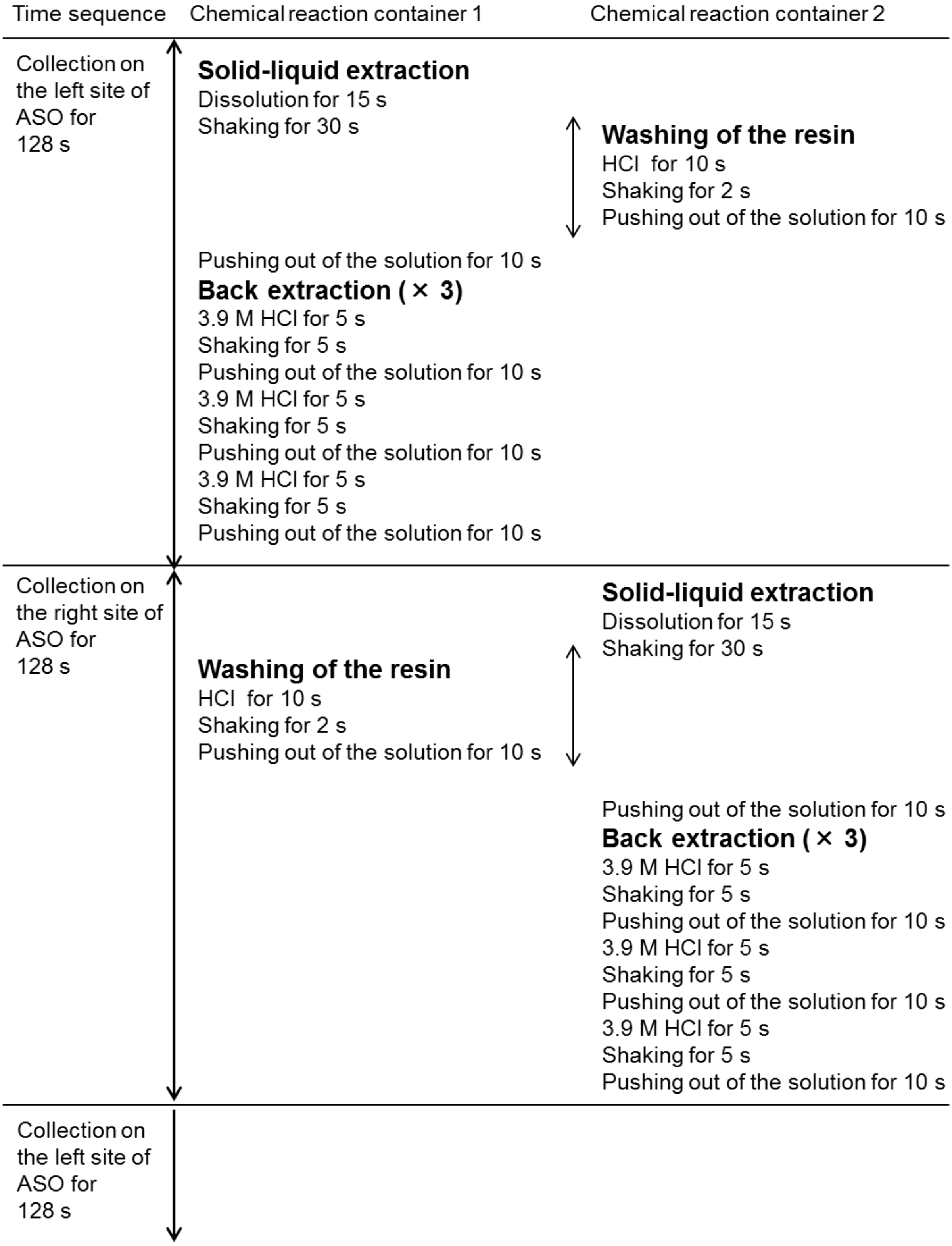


Figure 4-3. The time sequence of 30-s shaking control extraction experiment.



Time sequence	Chemical reaction container 1	Chemical reaction container 2
Collection on the left site of ASO for 133 s	**Solid-liquid extraction** Dissolution for 15 s Shaking for 10 s Pushing out of the solution for 10 s **Back extraction (× 3)** 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s **Washing of the resin** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s	
Collection on the right site of ASO for 133 s		**Solid-liquid extraction** Dissolution for 15 s Shaking for 10 s Pushing out of the solution for 10 s **Back extraction (× 3)** 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s **Washing of the resin** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s
Collection on the left site of ASO for 133 s		

Figure 4-4. The time sequence of 10-s shaking solid-liquid extraction experiment.



Time sequence	Chemical reaction container 1	Chemical reaction container 2
Collection on the left site of ASO for 128 s	**Solid-liquid extraction** Dissolution for 15 s Shaking for 30 s Pushing out of the solution for 10 s **Back extraction (× 3)** 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s	**Washing of the resin** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s
Collection on the right site of ASO for 128 s	**Washing of the resin** HCl for 10 s Shaking for 2 s Pushing out of the solution for 10 s	**Solid-liquid extraction** Dissolution for 15 s Shaking for 30 s Pushing out of the solution for 10 s **Back extraction (× 3)** 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s 3.9 M HCl for 5 s Shaking for 5 s Pushing out of the solution for 10 s
Collection on the left site of ASO for 128 s		

Figure 4-5. The time sequence of 30-s shaking solid-liquid extraction experiment.

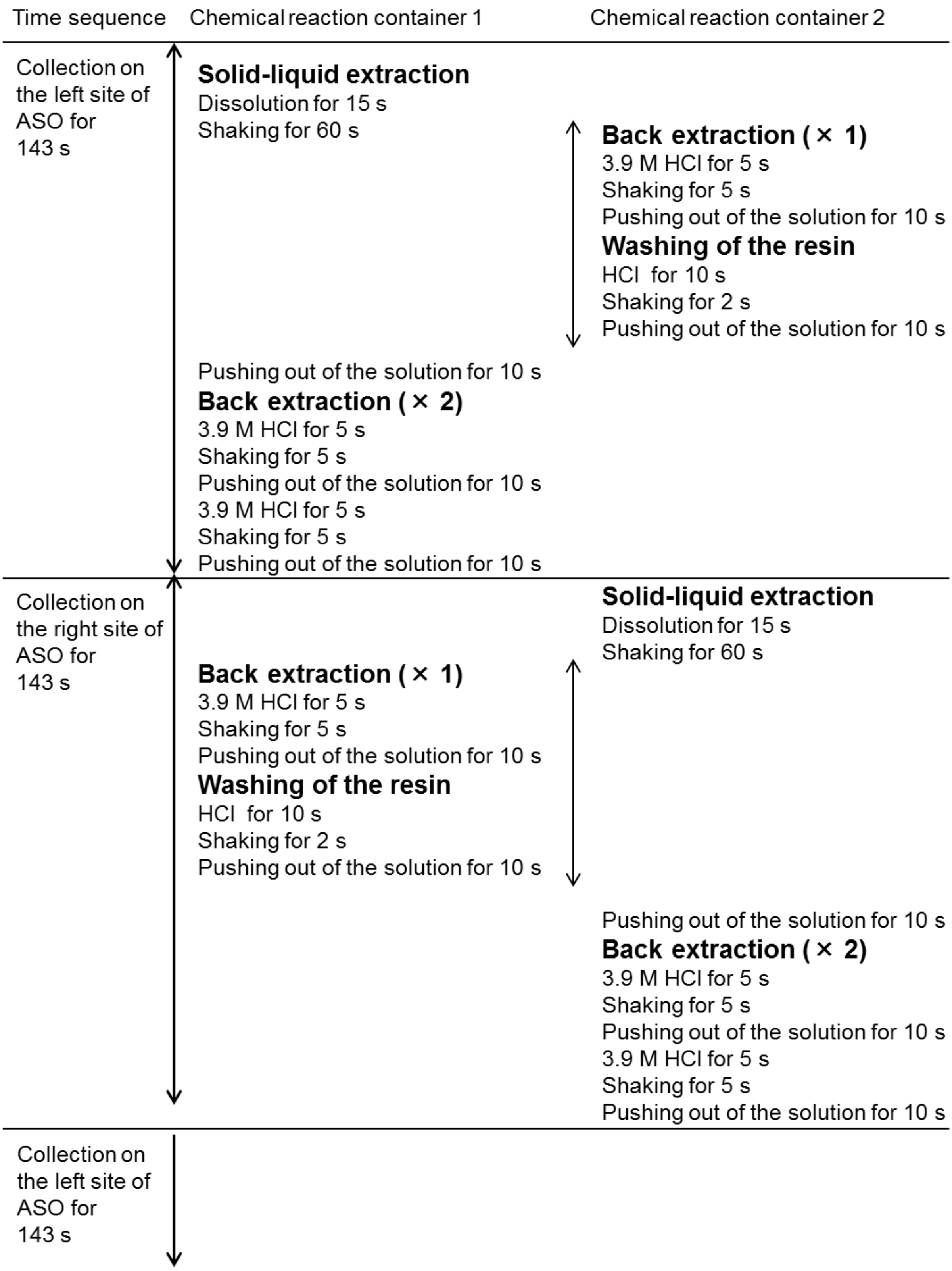


Figure 4-6. The time sequence of 60-s shaking solid-liquid extraction experiment.

Observed α counts of ^{261}Rf and its daughter ^{257}No are extremely low and can not become peaks. Therefore, α counts of ^{261}Rf are impossible to be distinguished from those of ^{257}No. Usually, all the α counts in the energy range of ^{261}Rf and ^{257}No are counted, and each α counts of ^{261}Rf and ^{257}No are calculated by taking into account the growth and decay of these nuclides.

In α-ray energy range of ^{261}Rf (E_α = 8.28 MeV)[108] and its daughter ^{257}No (E_α = 8.22, 8.32 MeV),[82] observed α-particles were categorized to three types: α-particles of ^{261}Rf (Rf), α-particles of ^{257}No reflected chemical property of Rf (Rf → No); ^{261}Rf was decay in the time interval between end of contact of two (solution and resin) phases and the start of counting, and α-particles of ^{257}No reflected chemical property of No (No); α-particles of ^{257}No existed in the extraction experiment. Figure 4-7 shows an example for time variation of the counts of ^{261}Rf and ^{257}No at 10-s shaking of control extraction experiment (cross section: 13 nb, beam intensity: 0.8 μA (particle), target thickness: 685.2 $\mu g/cm^2$). In this work, the counts of these nuclides were corrected assuming phase separation accomplished with 5 s, because phase separation procedure was completed with 10 s. In the section (d) in Figure 4-7, the total α-particle counts (N) were

$$N = N_{\mathrm{Rf}} + N_{\mathrm{Rf}\rightarrow\mathrm{No}} + N_{\mathrm{No}}. \tag{4-1}$$

The N_{Rf}, $N_{\mathrm{Rf}\rightarrow\mathrm{No}}$, and N_{No} were total detected counts of Rf, Rf → No, and No, respectively, and were following equations:

$$N_{\mathrm{Rf}} = \frac{A_{\mathrm{Rf}}\{1-\exp(-\lambda_{\mathrm{Rf}} t_{\mathrm{m}})\}}{\lambda_{\mathrm{Rf}}}, \tag{4-2}$$

$$N_{\mathrm{Rf}\rightarrow\mathrm{No}} = \frac{A_{\mathrm{Rf}}\lambda_{\mathrm{No}}\{1-\exp(-\lambda_{\mathrm{Rf}} t_{\mathrm{m}})\}}{\lambda_{\mathrm{Rf}}(\lambda_{\mathrm{No}}-\lambda_{\mathrm{Rf}})} - \frac{A_{\mathrm{Rf}}\{1-\exp(-\lambda_{\mathrm{No}} t_{\mathrm{m}})\}}{\lambda_{\mathrm{No}}-\lambda_{\mathrm{Rf}}} + \frac{A_{\mathrm{Rf}\rightarrow\mathrm{No}}\{1-\exp(-\lambda_{\mathrm{No}} t_{\mathrm{m}})\}}{\lambda_{\mathrm{No}}}, \tag{4-2}$$

$$N_{\mathrm{No}} = \frac{A_{\mathrm{No}}\{1-\exp(-\lambda_{\mathrm{No}} t_{\mathrm{m}})\}}{\lambda_{\mathrm{No}}}, \tag{4-3}$$

where A and t_{m} are counting rate at the end of phase separation and average of measurement time (s), respectively. In the section (c) in Figure 4-7, the A values of Rf, Rf→No, and No are obtained from following equations:

$$A_{\mathrm{Rf}} = A_{0\mathrm{Rf}} \exp(-\lambda_{\mathrm{Rf}} t_{\mathrm{d}}), \tag{4-5}$$

$$A_{\mathrm{Rf}\to\mathrm{No}} = \frac{\lambda_{\mathrm{No}} A_{\mathrm{eRf}} [\{\exp(-\lambda_{\mathrm{Rf}} (t_{\mathrm{d}} - t_{\mathrm{e}})\} - \exp\{-\lambda_{\mathrm{No}} (t_{\mathrm{d}} - t_{\mathrm{e}})\}]}{\lambda_{\mathrm{No}} - \lambda_{\mathrm{Rf}}} + A_{\mathrm{eRf\text{-}No}} \exp\{-\lambda_{\mathrm{No}} (t_{\mathrm{d}} - t_{\mathrm{e}})\}, \tag{4-6}$$

$$A_{\mathrm{No}} = A_{\mathrm{eNo}} \exp\{-\lambda_{\mathrm{No}} (t_{\mathrm{d}} - t_{\mathrm{e}})\}. \tag{4-7}$$

The A_{e} is counting rate of nuclide at the start of extraction experiments, the t_{d} is elapsed time from the start of the dissolution of the transported products to the start of the α-particle measurement, and the t_{e} is that from the start of the dissolution of the products to the start of the extraction experiment. In the section (b) in Figure 4-7, the A_{e} values of Rf, Rf→No, and No are described by

$$A_{\mathrm{eRf}} = A_{0\mathrm{Rf}} \exp(-\lambda_{\mathrm{Rf}} t_{\mathrm{e}}), \tag{4-8}$$

$$A_{\mathrm{eRf}\to\mathrm{No}} = 0, \tag{4-9}$$

$$A_{\mathrm{eNo}} = \frac{\lambda_{\mathrm{No}} A_{0\mathrm{Rf}} \{\exp(-\lambda_{\mathrm{Rf}} t_{\mathrm{e}}) - \exp(-\lambda_{\mathrm{No}} t_{\mathrm{e}})\}}{\lambda_{\mathrm{No}} - \lambda_{\mathrm{Rf}}} + A_{0\mathrm{No}} \exp(-\lambda_{\mathrm{No}} t_{\mathrm{e}}), \tag{4-10}$$

where A_0 is counting rate at the start of the dissolution of the products. The counts of ^{261}Rf ($N_{0\mathrm{Rf}}$) and ^{257}No ($N_{0\mathrm{No}}$) at the end of irradiation are described by

$$N_{0\mathrm{Rf}} = \frac{f\sigma N_{\mathrm{Cm}} \{1 - \exp(-\lambda_{\mathrm{Rf}} t)\}}{\lambda_{\mathrm{Rf}}}, \tag{4-11}$$

$$N_{0\mathrm{No}} = \frac{f\sigma N_{\mathrm{Cm}}}{\lambda_{\mathrm{No}}} - \frac{f\sigma N_{\mathrm{Cm}} \exp(-\lambda_{\mathrm{Rf}} t)}{\lambda_{\mathrm{No}} - \lambda_{\mathrm{Rf}}} + \frac{f\sigma N_{\mathrm{Cm}} \lambda_{\mathrm{Rf}} \exp(-\lambda_{\mathrm{No}} t)}{(\lambda_{\mathrm{No}} - \lambda_{\mathrm{Rf}}) \lambda_{\mathrm{No}}}, \tag{4-12}$$

where f is the flux density of the projectiles, σ is the cross section of nuclear reaction (13 nb),[10] and N_{Cm} is the number of the atoms of the target nuclide ^{248}Cm. The λ_{Rf} and λ_{No} are the decay constants of ^{261}Rf and ^{257}No, respectively. The t is irradiation time. In the section (a) in Figure 4-7, the A_0 values of Rf→No and No are

$$A_{0\mathrm{Rf}\rightarrow\mathrm{No}} = 0 , \tag{4-13}$$

$$A_{0\mathrm{No}} = A_{0\mathrm{Rf}} \frac{N_{0\mathrm{No}}}{N_{0\mathrm{Rf}}} . \tag{4-14}$$

Silva *et al.* reported that the No^{2+} ion was not extracted by trioctylamine chloride (anion exchanger) from 0.2–10.0 M HCl.[109] It was assumed that the No^{2+} ion is not adsorbed on the Aliquat 336 resin and is eluted with any solutions used in this experiment.

The asymmetric error limits of quotients ($Q = A_r/A_s$) of Rf were evaluated from the above counting statistics of the observed an event ratios based on the 68% confidence intervals for Poisson distributed values. The lower limit (Q_{lo} ($A_r \leq A_s$)) of a 68.3% confidence interval for a Q value (A_r/A_s) with $A_r \leq A_s$ is approximated with some percent error by

$$Q_{\mathrm{lo}}(A_{\mathrm{r}} \leq A_{\mathrm{s}}) = \frac{0.25 A_{\mathrm{r}}{}^{2}}{A_{\mathrm{s}}(1 + 0.25 A_{\mathrm{s}})} . \tag{4-15}$$

The width is approximated by

$$2\sigma = \frac{A_{\mathrm{r}}}{A_{\mathrm{s}}} \sqrt{\frac{1}{A_{\mathrm{r}}} + \frac{1}{A_{\mathrm{s}}}} . \tag{4-16}$$

The upper limit ($Q_{hi}(A_s \leq A_r)$) is given by

$$Q_{\mathrm{hi}}(A_{\mathrm{r}} \leq A_{\mathrm{s}}) = Q(A_{\mathrm{r}} \leq A_{\mathrm{s}}) + 2\sigma . \tag{4-17}$$

For $A_r > A_s$, one can use the reciprocals of the tabulated values and has to change the upper (Q_{hi} ($A_r > A_s$)) and lower limits (Q_{lo} ($A_r > A_s$)):

$$Q_{\mathrm{hi}}(A_{\mathrm{r}} > A_{\mathrm{s}}) = \frac{1}{Q(A_{\mathrm{r}} \leq A_{\mathrm{s}})} , \tag{4-18}$$

$$Q_{\mathrm{lo}}(A_{\mathrm{r}} > A_{\mathrm{s}}) = \frac{1}{Q_{\mathrm{hi}}(A_{\mathrm{r}} \leq A_{\mathrm{s}})} .^{110} \tag{4-19}$$

The Q_d values were determined by equation (2-2) in subsection 2.2.3. Control extraction experiments were performed with 10-s shaking at 7.9 and 9.0 M HCl and with 30-s shaking at 9.0 M

HCl. The counts of control extraction with 60-s shaking were calculated from the detected counts in that of control extraction experiment for 10-s shaking and the growth and decay of ^{261}Rf and ^{257}No.

To examine the time required to equilibrium in the extraction, the time dependences of the Q_d values were investigated in the range 10–60 s in 7.9 M HCl. In addition, the K_d values of Rf and Hf were determined in 7.9 and 9.0 M HCl.

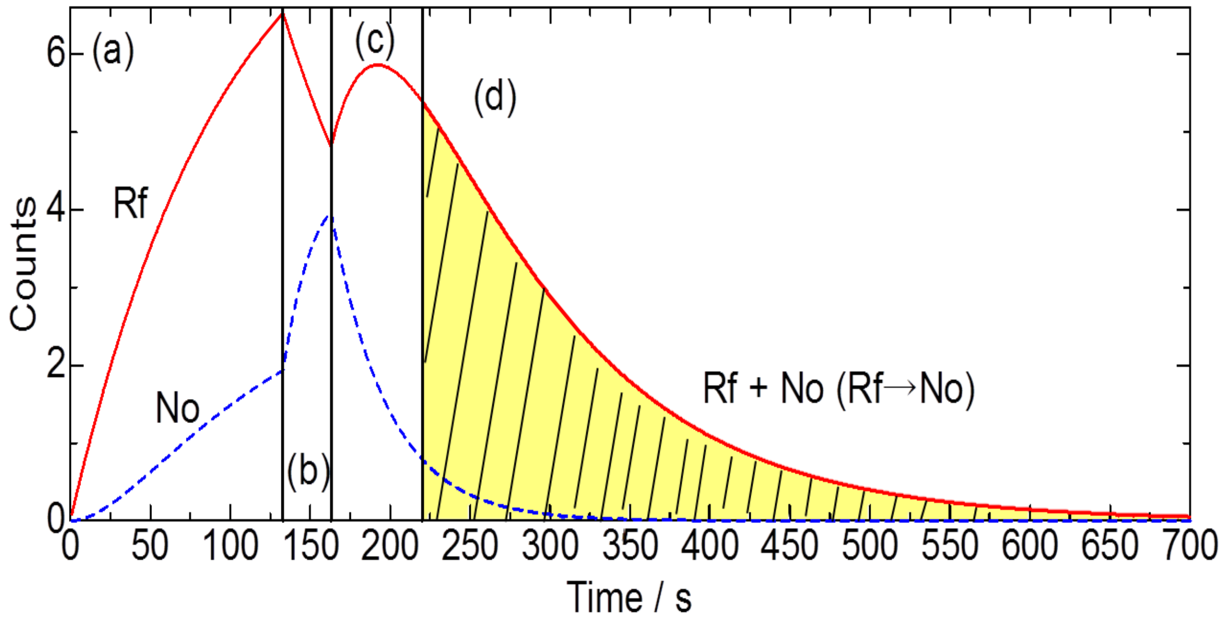


Figure 4-7. The time variation of counts of ^{261}Rf and ^{257}No at 10-s shaking of control extraction experiment. Solid line is Rf and No reflected chemical property of Rf, and dashed line is No reflected chemical property of No. The Sections (a) irradiation term, (b) chemical procedure (dissolution, solid-liquid extraction, and phase separation) term, (c) preparation of α-particle measurement term, and (d) measurement term are indicated. The α counts of section (d) are detected.

4.3 Results and Discussion

Figures 4-8(a) and (b) show α spectra of samples prepared from control extraction experiments with 10- (7.9 and 9.0 M HCl) and with 30-shaking (9.0 M HCl), respectively. Figures 4-8 (c)–(f) show α spectra of samples prepared from solid-liquid extraction experiments with 28 wt% Aliquat 336 resin for (c) 10-, (d) 30-, and (e) 60-s shaking in 7.9 M HCl, and (f) 10-s shaking in 9.0 M HCl. The α-lines from ^{150}Dy (E_α = 4.23 MeV), ^{151}Dy (E_α = 4.07 MeV), ^{248}Cm (E_α = 5.39, 5.34 MeV), ^{244}Cm (E_α = 5.80, 5.76 MeV), and ^{254}Fm (E_α = 7.19, 7.15 MeV) are detected. The α-ray spectra of ^{254}Fm had broadness in the range −50–300 keV, and the α peak of ^{254}Fm was 70–195 keV FWHM. In this study, an energy window from 7.91 to 8.43 MeV was selected to search for the α-decays of the ^{261}Rf (E_α = 8.28 MeV)[108] and its daughter ^{257}No (E_α = 8.22, 8.32 MeV),[82] including time correlated pairs of mother–daughter decays of these nuclides.

At the one shot experiment, the α event is estimated to be ~0.5 event in the ^{261}Rf and ^{257}No energy range. When two events are observed at the one shot experiment, expecting that one is ^{261}Rf event, and the other is ^{257}No event. To confirm the integrity of the α events of ^{261}Rf and ^{257}No, the ratio of α-single of ^{261}Rf and ^{257}No and α–α correlation from ^{261}Rf and ^{257}No in the experiment is compared with that in the calculation by taking into account the counting efficiency of the detector and the growth and decay of ^{261}Rf and ^{257}No.

The results of the control extraction experiments are summarized in Table 4-1, where the HCl concentration, the shaking time, .the total ^{18}O beam dose, the number of cycles of the extraction, the chemical yield determined by ^{169}Hf radioactivity measurements, the number of observed α particles of α-single and α–α correlation, and the ratio of α-single to α–α-correlations; the corresponding data for solid-liquid extraction experiments are shown in Table 4-2. The chemical yield of ^{169}Hf in the solid-liquid extraction from 9.0 M HCl was corrected, on the basis of 15% extraction of Hf with about 1 mg of 28 wt% Aliquat 336 resin. The chemical yield of ^{169}Hf was 29–56%. From the 379 cycles of the experiment, a total of 132 α events from ^{261}Rf and its daughter ^{257}No were registered in the energy range 7.91–8.43 MeV, including 23 time-correlated α pairs of ^{261}Rf and ^{257}No. The observed event ratios are reasonably consistent with estimated one in all the experimental conditions studied. The cross section of ^{261}Rf was evaluated to be 8 and 10 nb from the α-decay events in the control extraction experiment with 10 and 30 s of shaking with a 50% transport efficiency of the gas-jet system, respectively. These values were in agreement with previously reported value (13 nb).[10] The estimated half-life of ^{261}Rf was 62 s in the present study, which was agreement with reported value (68 s).[81] Thus, α events in the energy window from 7.91 to 8.43 MeV were certainly α events of ^{261}Rf and ^{257}No. An average background was evaluated to be 9.16×10^{-5} counts/s for each detector in the energy range 7.91–8.43 MeV.

The count rates of α event in the control extraction experiment with 30-s shaking were also calculated from that with 10-s shaking. The ratio of the calculation and the experiment of the count rate divided by the number of cycle of the experiment was 1.04, indicating that the calculated count of control extraction experiment with 60-s shaking is confidence.

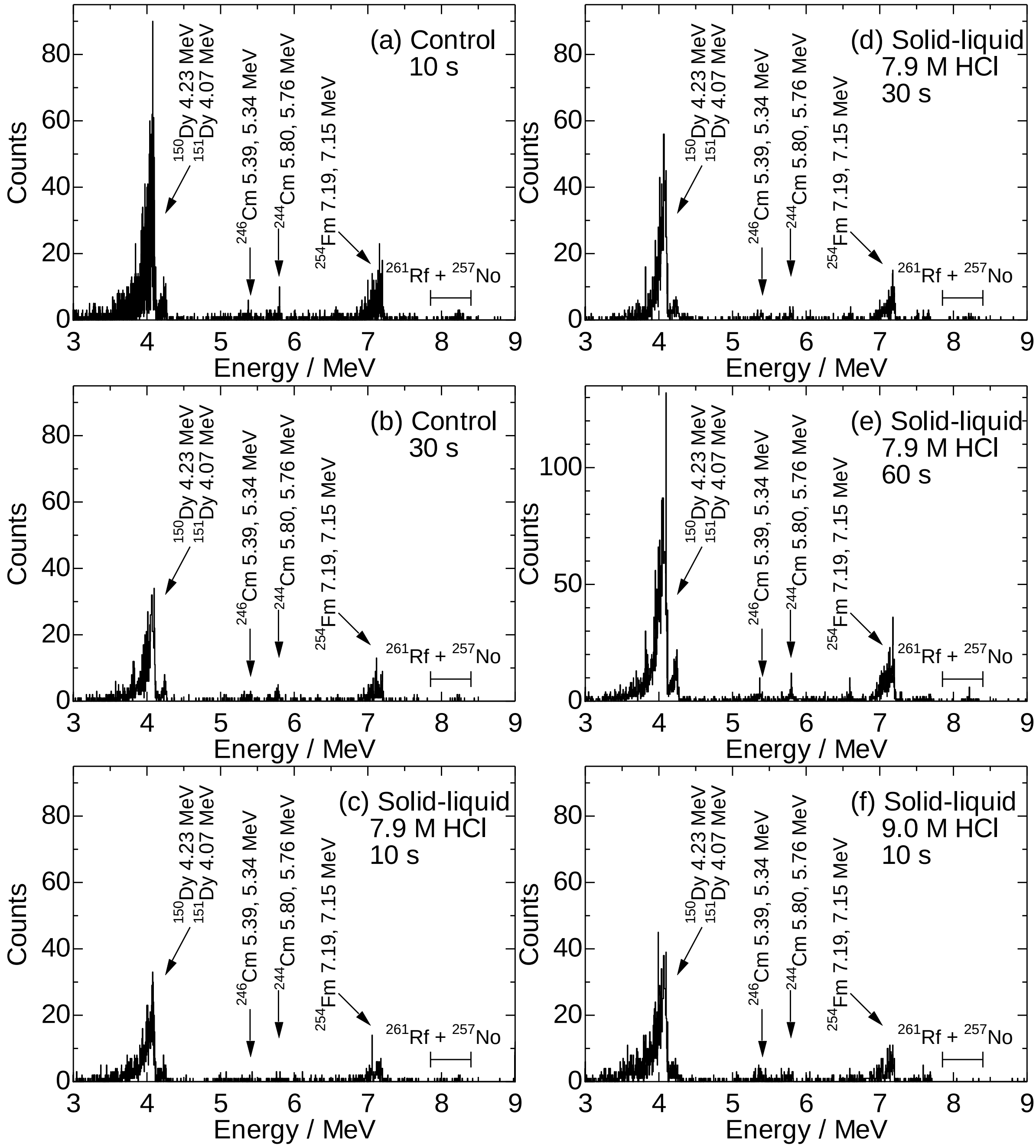


Figure 4-8. Alpha-particle spectra observed in (a) a control extraction experiment without resin in 7.9 and 9.0 M HCl with 10-s shaking (71 cycles), (b) a control extraction experiment without resin in 7.9 and 9.0 M HCl with 30-s shaking (47 cycles), (c) a solid-liquid extraction experiment with 28 wt% Aliquat 336 resin in 7.9 M HCl with 10-s shaking (38 cycles), (d) a solid-liquid extraction experiment with 28 wt% Aliquat 336 resin in 7.9 M HCl with 30-s shaking (50 cycles), (e) a solid-liquid extraction experiment with 28 wt% Aliquat 336 resin in 7.9 M HCl with 60-s shaking (105 cycles), and (f) a solid-liquid extraction experiment with 28 wt% Aliquat 336 resin in 9.0M HCl with 10-s shaking (68 cycles).

Table 4-1. Summary of on-line experiments of Rf with a control extraction experiment without the resin

[HCl] / M	Shaking time / s	Total beam dose $\times 10^{17}$	Number of cycle of the experiment	Average chemical yield of ^{169}Hf / %	α-count		α/α−α	
					α	α-α	experiment	calculation
7.9, 9.0	10	1.237	71	45	38	7	5.4	7.3
9.0	30	0.786	47	29	12	2	6.0	7.3

Table 4-2. Summary of on-line experiments of Rf with a solid-liquid extraction experiment with 28 wt% Aliquat 336 resin

[HCl] / M	Shaking time / s	Total beam dose $\times 10^{17}$	Number of cycle of the experiment	Average chemical yield of ^{169}Hf / %	α-count		α/α−α	
					α	α-α	experiment	calculation
7.9	10	0.679	38	56	24	6	4.0	7.3
7.9	30	0.849	50	52	21	3	7.0	7.4
7.9	60	1.842	105	43	34	5	6.8	7.5
9.0	10	1.201	68	47	3	0	–	15.1

[a] The chemical yield of ^{169}Hf was corrected, on the basis of 15% extraction of Hf with about 1 mg of 28 wt% Aliquat 336 resin.

The dependences of the Q_d values of Rf and Hf on the shaking time in the extraction with 28 wt% Aliquat 336 resin are shown in Figures 4-9(a) and (b), respectively. The Q_d values of Rf and Hf remain roughly constant, indicating that extraction equilibrium was established within 10 s. In this chemical reaction system, times required to reach equilibrium for Rf as well as Zr and Hf was very short. This is the first investigation of the time dependency of the Q values of transactinide on an atom-at-a-time basis. According to extraction equilibrium within 10 s in 7.9 M HCl, extraction experiment was performed with only 10-s shaking in 9.0 M HCl (higher than 7.9 M of Cl^- concentration).

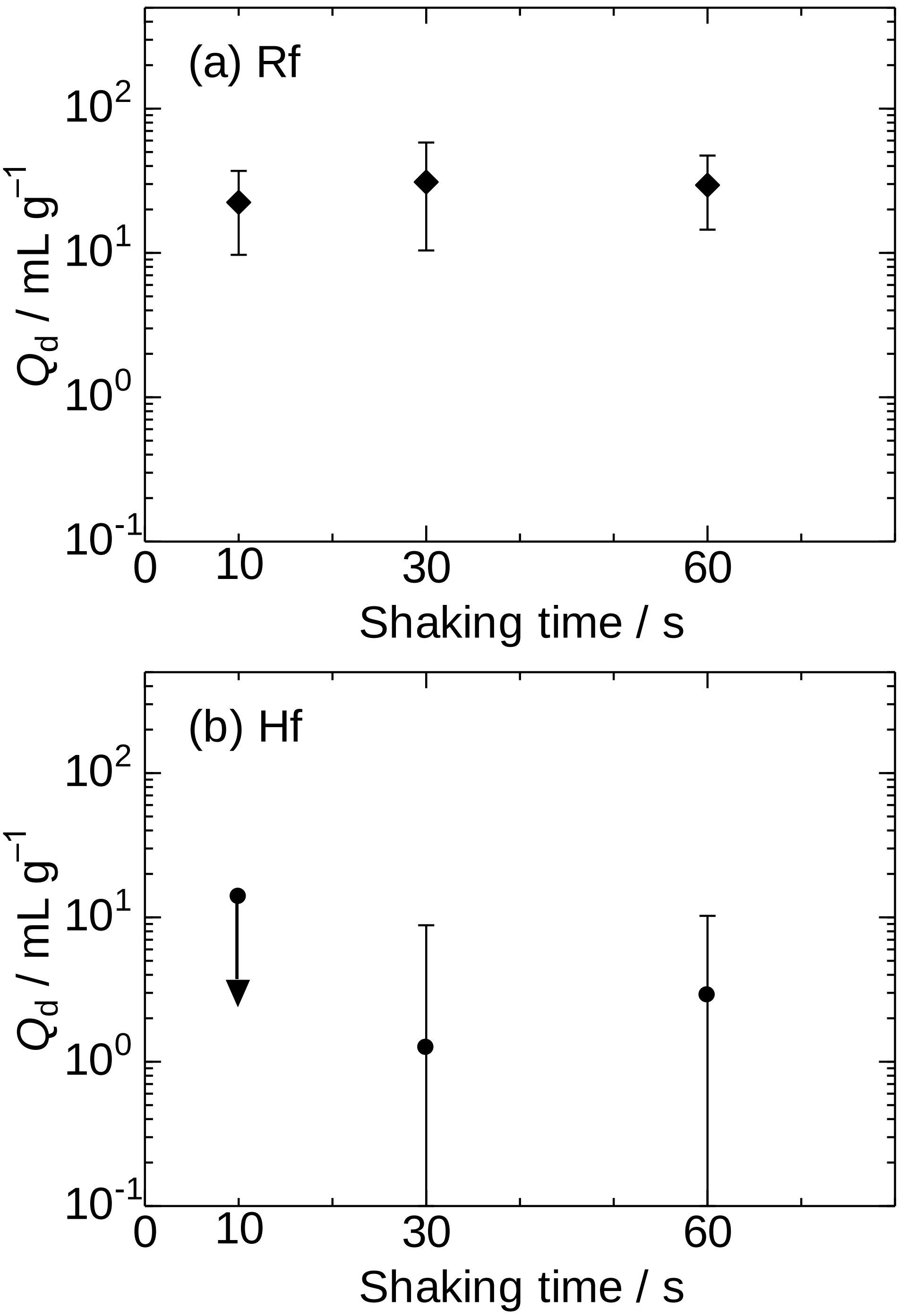


Figure 4-9. The Q_d values of (a) Rf and (b) Hf for different shaking times in 7.9 M HCl with 28 wt% Aliquat 336 resin. Arrow shows the upper limit of the K_d value of Hf. The solid-liquid extraction experiment were carried out with 10-s shaking (38 cycles), 30-s shaking (50 cycles), and 60-s shaking (105 cycles).

The dependence of the K_d values of Rf and Hf on the HCl concentration in the extraction with 28 wt% Aliquat 336 resin are shown in Figure 4-10, together with the Zr, Hf, and Th data in the off-line (subsections 2.1.3) and the on-line (subsection 3.3.2) experiments. In 9.0 M HCl, the K_d value of Hf obtained in the on-line Rf experiment is consistent with that in the off-line experiment. A lower limit for the K_d value of Rf > 1592 mL g^{-1} (95% confidence) was obtained in 9.0 M HCl. The K_d value of Rf in 9.0 M HCl was higher than that in 7.9 M HCl, indicating that the abundance of the anionic chloride complexes of Rf increases with an increase of the HCl concentration similarly to the case for Zr and Hf and differently to the case for Th. The same tendencies were already reported,[24,40] although it is not clear whether these distribution reactions of Rf reached equilibria from this study. The K_d value of Rf was similar to that of Zr in 7.9 M HCl, while that of Rf was higher than at least one order that of Zr and two order that of Hf in 9.0 M HCl. The clear difference of the K_d values between Rf, Zr, and Hf was first observation. Previously, at 80 °C in anion exchange (not clear whether anion-exchange reaction reached equilibrium), percent adsorption was in the sequence of Rf > Zr > Hf,[38] and the sequence was consistent with the sequence of K_d values in this work. The order of the K_d values in 9.0 M HCl, was different from that in the anion exchange of fluoride complex (Zr ≈ Hf > Rf » Th).[30,36,37,41,45] Although the sequence of the K_d values in fluoride complex was reverse order of the ionic radii (ionic radii with the coordination number of 6 are in the order of Hf: 71 pm [103] ≈ Zr: 72 pm [103] < Rf: 79 pm [3] « Th: 94 pm [103]), those in chloride complex was non-related with the ionic radii. According to EXAFS spectroscopy study in 9.0–11.9 M HCl, the Zr and Hf species exists as $[MCl_6]^{2-}$ (M = Zr and Hf), and the difference in the K_d values of Zr and Hf is attributed to the different stability of their chemical species.[80] If the extracted species of Rf is $[RfCl_6]^{2-}$ (the same configuration as those of Zr and Hf), the affinity of Cl^- ion for the group 4 metal ions (see equation (2-8)) is in the following sequence Rf > Zr > Hf from the present result. In another possibility, the difference in the K_d values between Rf and the homologues would be due to the chemical configurations such as Rf-oxochloride complexes such as $[Rf(OH)Cl_5]^{2-}$ and/or their net charges involved such as $[RfCl_7]^{3-}$. In the present work, the including net charges were not able to be identified.

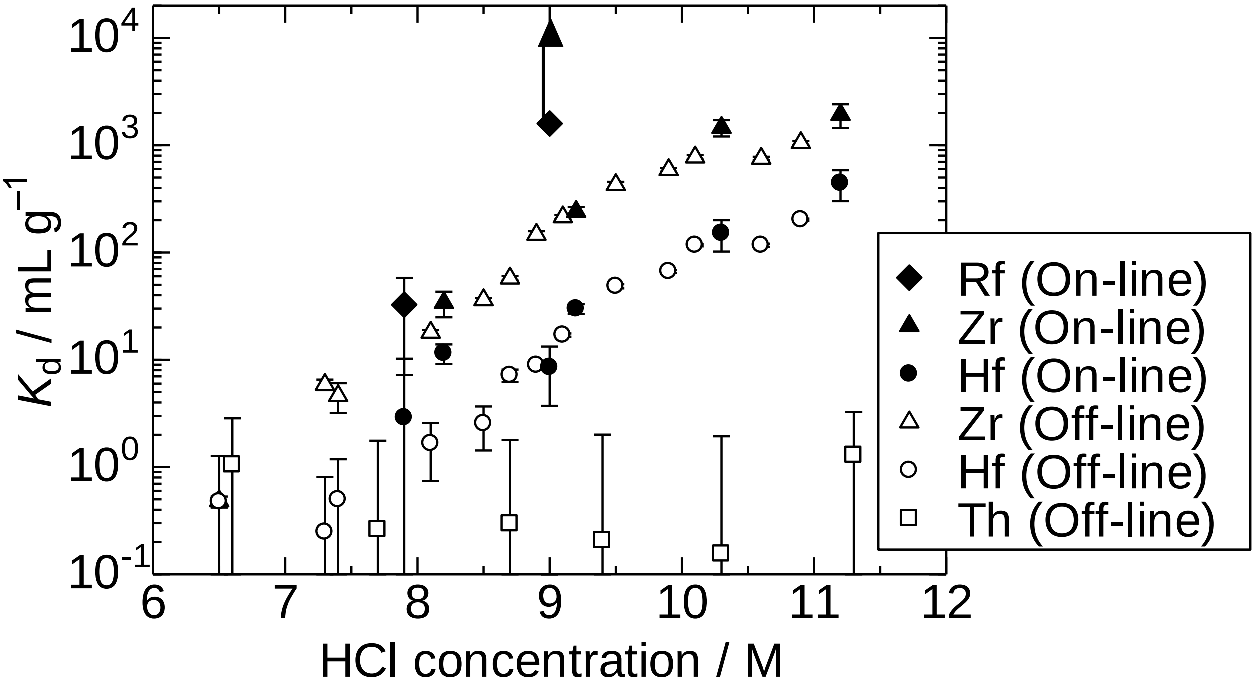


Figure 4-10. The K_d values of Rf, Zr, Hf, and Th as a function of the HCl concentration with 28 wt% Aliquat 336 resin. Arrow shows the lower limit of the K_d value of Rf.

4.4 Conclusion

By using AMBER, on-line solid-liquid extraction experiment by Aliquat 336 resin from HCl was successfully performed for ^{261}Rf produced by the accelerator at RIKEN. The Q_d values of Rf were constant from 10–60 s in 7.9 M HCl; similarly to the cases for Zr and Hf indicating that the equilibrium was established within 10 s. This is the first observation of time dependency of the chemical behavior of transactinides, and the rapid equilibration of the extraction reactions for Rf was observed. In addition, the HCl concentration dependence on the K_d values of Rf were investigated. The K_d values of Rf increased as the HCl concentration increased, suggesting the formation of anionic chloride complexes of Rf as well as Zr and Hf. In 9.0 M HCl, the K_d value of Rf was clearly higher than that of Zr and Hf, which was attributed to the higer stability of their chemical species, or different chemical configurations, and/or higher net charges.

Chapter 5. Comprehensive Discussion

Solid-liquid extraction of group 4 (Zr, Hf, and Th) and group 5 (Nb, Ta, and Pa) elements in the Aliquat 336/HCl system were performed under the off-line condition (Chapter 2). The extraction reactions of group 4 elements reached equilibrium with shaking for 10 s (Subsection 2.1.3). Those of group 5 elements, however, reached equilibrium for Nb and Pa after 10-s shaking, yet required 2–3 h for Ta (Subsection 2.2.3). For example, in the cation exchange of Zr and Hf in H_2SO_4/HNO_3, the reaction kinetics was different between Zr and Hf.[48] Therefore, it is important to investigate the time dependence of the distribution behaviors of transactinides for the acquisition of their equilibrated data, because the time required to reach distribution equilibrium may be different among homologues.

In this study, the time dependence of the Q_d values of Rf was investigated in the solid-liquid extraction with 28 wt% Aliquat 336 resin from 7.9 M HCl using the presently developed batch-type solid-liquid extraction apparatus, AMBER. This is the first investigation of the time dependency of the distribution behavior of transactinide in atom-at-a-time basis. The results in this experiment revealed that the extraction reactions of Rf reached equilibrium within 10 s as well as Zr, Hf, and Th. The K_d value in equilibria of Rf in 9 M HCl was clearly higher than those of Zr and Hf (Section 4.3). In the present study, the reason for the difference in the K_d values between Rf, Zr, and Hf was not clarified, although some reasons were given. In the future, to study detailed chloride complex formation of Rf, HCl and Aliquat 336 concentration dependences of the K_d values of Rf are needed to investigate. In a similar manner, Rf experiments in another inorganic ligands such as HBr, H_2SO_4, and HNO_3 would be feasible. A various complex formation for transactinide study method was established in this work.

The observation of the extraction equilibrium of Db is interesting, because the time required for extraction equilibrium is different between Nb, Ta, and Pa in the Aliquat 336/HCl system. In the same method as that for Rf experiment with 10-s shaking using AMBER, the event rate of ^{262}Db and ^{258}Lr is estimated to be only 8.2 events/day (Subsection 2.2.3). Thus, 3-days beam time is needed for the experiment with Db for 1 condition. Db experiment is needed to be performed by faster method and with higher chemical yield than those for Rf experiment, because ^{262}Db is lower production rate (cross section: 2.1 nb)[106] and shorter half-life (34 s) than ^{261}Rf (cross section: 13 nb,[10] half-life: 68 s). In the present experimental condition, nuclear reaction products are dissolved and entered chemical reaction container of AMBER with 15 s, and the 0.25 mL of solution sample are evaporated to dryness for about 40 s. From previous study of our research group, dissolved nuclear reaction products could be eluted within 8 s below ASO (Appendix 3). If reaction products entered chemical reaction container with 8 s (solution volume: 0.13 mL), evaporation time is also able to be shorten. Therefore, to evaluate the time dependence of distribution behavior of Db, reducing the dead volume for AMBER is needed. By the impressment of the accelerator performance, production rates of transactinides are also rising.

The element 103 (Lr), which is last element of actinide series, experiment would be carried out. The ^{256}Lr nuclide ($T_{1/2}$ = 28 s) is produced in the ^{248}Cm(^{14}N,6n)^{256}Lr reaction. The cross section is 27 nb with ^{14}N projectile with energy of 91 MeV.[111] In the bombardment of 685.2 μg/cm^2 of ^{248}Cm with ^{14}N beam (beam current: 0.8 particle-μA, gas-jet transport efficiency: 50%, the efficiency of detector: 34%), the event rate of ^{257}Lr is estimated to be 15 events/day (cycle time: 133 s, sample preparation time: 87 s, number of cycle: 400 times). Thus, 2-days beam time is needed for the experiment with Lr for 1 condition.

In the future, by using AMBER, the validity of atom-at-a-time basis chemistry might be able to be verified in the on-line experiment. Namely, atom number dependency of the distribution behavior would be observed. An example is the solid-liquid extraction experiment of element 101, mendelevium (Md) from HCl with di(2-ethylhexyl)-phosphoric acid (HDEHP) resin. The ^{255}Md nuclide ($T_{1/2}$ = 27 min) is produced in the ^{248}Cm(^{11}B,4n)^{255}Md reaction. The cross section is 4000 nb with ^{11}B projectile with energy of 58 MeV.[112] The production rate of ^{255}Md is significantly higher than those of transactinide nuclides. In the bombardment of 500 μg of ^{248}Cm with ^{11}B beam (beam current: 0.5 particle-μA, irradiation time: 10 min, gas-jet transport efficiency: 50%, dissolution yield: 50%), Md in the chemical reaction container of AMBER is estimated to be ~2000 atoms. In this case, after 30-min shaking, the number of ^{255}Md nuclide is in the 10^3 order. Production rates of ^{255}Md were changed by beam current, amounts of target, and irradiation time. As a result, experiments of ^{255}Md can performed at single–several thousands atom levels. However, in the single atom level, the detection of α counts of ^{255}Md is extremely low, because α-branch of ^{255}Md is only 8%. On the other hand, the nuclide of ^{255}No ($T_{1/2}$ = 3.1 min) is produced in the ^{248}Cm(^{12}C,5n) reaction. The cross section is 580 nb with ^{12}C with energy of 77.8 MeV.[113] Experiment using ^{255}No can performed at single–several hundreds atom levels. Therefore, dependence of the K_d on the number of the atom might be able to be investigated using AMBER.

Chapter 6. Summary

To evaluate time dependencies of the distribution behavior of Rf and Db and study distribution behaviors of Rf and Db in chemical reaction equilibrium, following studies were performed.

Solid-liquid extraction of Zr, Hf (homologues), and Th (pseudo homologue) was carried out in the Aliquat 336/HCl system by off-line batch method for Rf experiments. From the time dependencies of the Q_d values of these elements, it was found that the extraction reactions reached equilibrium with shaking for 10 s, indicating that this extraction system is suitable for Rf experiment. The dependences of the K_d values of Zr, Hf, and Th on the HCl concentration indicates that the Zr and Hf form anionic chloride complexes, while the Th does not form anionic species. In this study, comparison data for Rf to discuss its chemical condition were obtained.

Distribution behaviors of Nb, Ta (homologues), and Pa (pseudo homologue) were investigated in cation-exchange adsorption and solid-liquid extraction by Aliquat 336 from HCl by off-line batch method for Db experiments. The dependences of the Q_d values of these elements on the shaking time were studied. Chemical reactions in the cation exchange reached equilibrium within 10 s of shaking. Extraction reactions with Aliquat 336 reached equilibrium within 10 s for Nb and Pa, while those reached 2–3 h for Ta. Therefore, it was found that time dependence of the distribution behavior of Db is interesting. Dependencies of the K_d values on the HCl and Aliquat 336 concentrations were investigated. The dominant Nb species are neutral in 0.1–4 M HCl and anionic in 4–11 M HCl. For Ta, dominant chemical species are cationic in 0.08–0.5 M HCl, neutral in 0.5–5 M HCl, and anionic in 5–11 M HCl. The Pa species are cationic in 0.1–2 M HCl, neutral in 2–3 M HCl, and anionic in 3–11 M HCl. The different chemical configuration between Nb, Ta, and Pa were formed, and chemical species of Db were interesting. From this study, comparison data for Db were obtained.

A new chemical reaction container of batch-type solid-liquid extraction apparatus, AMBER, was developed, and working of AMBER was also changed. By these improvements, the liquid spill and reflux at chemical reaction container were prevented, and, therefore, AMBER was achieved development. Back extraction behavior of the adsorbed Zr and Hf on the 28–48 wt% Aliquat 336 resin was investigated. The 28 wt% Aliquat 336 resin was found to be suitable for Rf experiment. By using AMBER, the on-line solid-liquid extraction experiment of Zr and Hf at RCNP was performed, and the experimental condition for Rf was determined. The K_d values of Zr and Hf in the on-line experiment were agreement with those in the off-line experiment except for Hf in 8.2 M HCl. The solid-liquid extraction in the Aliquat 336/HCl system using AMBER would be applicable to Rf experiment.

By using AMBER, solid-liquid extraction of Rf in the Aliquat 336/HCl system was performed. From the time dependency of the Q_d values of Rf in 7.9 M HCl with 28 wt% Aliquat 336 resin, the extraction reaction of Rf as well as Zr and Hf reached equilibrium within 10 s. In this study, chemical reaction equilibrium for transactinide elements was observed for the first time. The K_d values of Rf was increased in increasing HCl concentration similarly to the case for Zr and Hf and differently to the case for Th. The K_d value of Rf was equivalent to the values of Zr in around 8 M HCl, while that of Rf in 9 M HCl was higher than one order that of Zr and two order that of Hf in 9 M HCl. It is indicated that the chloride complex formations were clearly different among group 4 elements. In the present study, the reason for the difference in the K_d values between Rf, Zr, and Hf was not clarified. Reasons for this were considered different chemical configurations and/or net charges. To study detailed chloride complex formation of Rf, the extraction behaviors of Rf in various HCl and Aliquat 336 concentrations are needed to study.

I believe that the AMBER would be feasible for the investigation on the distribution behaviors and equilibrium of Rf and Db in various chemical reaction systems and verify chemical reaction equilibrium in atom-at-a-time basis chemistry in the future.

Acknowledgment

I express my sincere gratitude to Prof. Dr. Atsushi Shinohara (Graduate School of Science, Osaka University) for his constant support, direction, and encouragement throughout the course of this study.

I would like to acknowledge to thank Prof. Dr. Satoshi Tsukahara (Graduate School of Science, Osaka University) for his advices and interest in this thesis. I would like to be thankful to Prof. Dr. Naoto Ishikawa (Graduate School of Science, Osaka University) for his enlightening instrthem advives and interest in my thesis.

I would like to especially express my gratitude to Dr. Yoshitaka Kasamatsu (Graduate School of Science, Osaka University) for his pertinent suggestion, interesting discussions, kind guidance, support on the experiments, and patient proofreading of my published papers and this thesis.

I am grateful to Dr. Naruto Takahashi (Graduate School of Science, Osaka University) for support of experiments at RCNP and advice. I am also thankful to Dr. Kazuhiko Ninomiya (Graduate School of Science, Osaka University) for his helpful advice on my investigation.

I am grateful to graduate and fellow students in Laboratory of Radiochemistry (Graduate School of Science and School of Science, Osaka University) I would like to express to Mr. Kouhei Nakamura for advice, development and setup of ASO, and support on the various experiments. I would like to express to Ms. Aiko Kino for advice, development of AMBER, and purification of ^{88}Zr and ^{175}Hf tracers. I would like to express to Dr. Yukiko Komori for support on the on-line experiments and her discussion. I would like to express to Mr. Yudai Shigekawa for advice, support on the on-line experiments. I would like to express to Mr. Yuuki Yasuda for advice and support on the on-line experiments. I would like to express to Mr. Keigo Toyomura advice and support on the on-line experiments.

I would like to express to acknowledgement to Prof. Dr. Takashi Yoshimura (Radioisotope Research Center, Osaka University) for his discussion and proofreading of my published papers.

I would like to express experiments at RIKEN to fellow in RI Application Team, RIKEN

Nishina Center for Accelerator-Based science. I would like to express acknowledgement to Dr. Hiromitsu Haba for support on the on-line experiments, his valuable advice. I would like to thankful to Mr. Masashi Murakami for support on the on-line experiments and sample preparation of ^{212}Bi–^{212}Po. I would like to thankful to Mr. Jumpei Kanaya for support on the on-line experiment. I am also thankful to Dr. Minghui Huang for support on the on-line experiment.

I express my gratitude to the accelerator crew of RCNP for the production of ^{88,89g,m}Zr, ^{173,175}Hf, ^{95}Nb, and ^{177,179}Ta. I express my gratitude to the staff of the RI Beam Factory for the production of ^{261}Rf and ^{169}Hf. I also thank the staff of Machine Shop (Center for Scientific Instrument Renovation and Manufacturing Support, Osaka University), for the making of dissolution equipment and batch-type solid-liquid extraction apparatus.

I would like to express acknowledgements to Ms. Kanako Kawase (Graduate School of Science, Osaka University) for her supports and encouragements. I also wish to acknowledgements with many graduate and fellow students in Laboratory of Radiochemistry (Graduate School of Science and School of Science, Osaka University), Ms. Mai Eguchi, Mr. Kazuya Fujihara, Mr. Yoshihiko Hayashi, Dr. Hayato Ikeda, Mr. Makoto Inagaki, Mr. Shunsuke Kakitani, Ms. Shizuka Matsunaga, Mr. Keisuke Morimoto, Mr. Naoya Shiohara, Mr. Yuji Osumi, Mr. Felix Riexinger, Ms. Moe Seike, Mr. Tatsuki Shiroyama, Mr. Sven Warfsmann, Mr. Ryosuke Yasui, Mr. Go Yoshida, and Mr. Jian Zhang Zi, for their supports and encouragements.

I would like to express my collaborators of other study. I am grateful to Dr. Kazuhiro Ooe (Faculty of Science, Niigata University) for his discussion. I would like to thankful to Dr. Koichi Takamiya (Research Reactor Institute, Kyoto University) for production and purification of multitracer.

References

1. Yu. Ts. Oganessian, F. Sh. Abdullin, P. D. Baieley, D. E. Benker, M. E. Bennett, S. N. Dmitriev, J. G. Ezold, J. H. Hamilton, R. A. Henderson, M. G. Itkis, Yu. V. Lobanov, A. N. Mezentsev, K. J. Moody, S. L. Nelson, A. N. Polyakov, C. E. Porter, A. V. Ramayya, F. D. Riley, J. B. Roberto, M. A. Ryabinin, K. P. Rykaczewski, R. N. Sagaidak, D. A. Shaughnessy, I. V. Shirokovsky, M. A. Stoyer, V. G. Subbotin, R. Sudowe, A. M. Sukhov, Yu. S. Tsyganov, V. K. Utyonkov, A. A. Voinov, G. K. Vostokin, P. A. Wilk, *Phys. Rev. Lett.* **2010**, *104*, 142502.
2. M. Schädel, *Angew. Chem. Int. Ed.* **2006**, *45*, 368.
3. *The Chemistry of Superheavy Elements*, 2nd edn. ed. By M. Schädel, D. Shaughnessy, Springer: Heidelberg **2014**.
4. A. Türler, V. Pershina, *Chem. Rev.* **2013**, *113*, 1237.
5. V. Pershina, *Radiochim. Acta* **2011**, *99*, 459.
6. K. S. Pitzer, *J. Chem. Phys.* **1975**, *63*, 1032.
7. Yu. Ts. Oganessian, *Radiochim. Acta.* **2011**, *99*, 429.
8. S. Hofmann, G. Münzenberg, *Rev. Mod. Phys.* **2000**, *72*, 733.
9. K. Morita, K. Morimoto, D. Kaji, H. Haba, K. Ozeki, Y. Kudou, T. Sumita, Y. Wakabayashi, A. Yoneda, K. Tanaka, S. Yamaki, R. Sakai, T. Akiyama, S. Goto, H. Hasebe, M. Huang, T. Huang, E. Ideguchi, Y. Kasamatsu, K. Katori, Y. Kariya, H. Kikunaga, H. Koura, H. Kudo, A. Mashiko, K. Mayama, S. Mitsuoka, T. Moriya, M. Murakami, H. Murayama, S. Namai, A. Ozawa, N. Sato, K. Sueki, M. Takeyama, F. Tokanai, T. Yamaguchi, A. Yoshida, *J. Phys. Soc. Jpn.* **2012**, *81*, 103201.
10. Y. Nagame, *J. Nucl. Radiochem. Soc.* **2005**, *6*, A21.
11. R. Guillaumont, J. P. Adloff, A. Penelox, *Radiochim. Acta* **1989**, *46*, 169.
12. R. Silva, J. Harris, M. Nurmia, K. Eskola, A. Ghiorso, *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 871.
13. I. Zváea, V. Z. Belov, L. P. Chelnokov, V. P. Domanov, M. Hussonois, Yu. S. Korotkin, V. A. Schegolev, M. R. Shalayevsky, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1109.
14. K. E. Gregorich, R. A. Henderson, D. E. Lee, M. J. Nurmia, R. M. Chasteler, H. L. Hall, D. A. Bennett, C. M. Gannett, R. B. Chadwick, J. D. Leyba, D. C. Hoffman, G. Herrmann, *Radiochim. Acta* **1988**, *43*, 223.
15. M. Schädel, W. Brüchle, R. Dressler, B. Eichler, H. W. Gäggeler, R. Günther, K. E. Gregorich, D. C. Hoffman, S. Hübener, D. T. Jost, J. V. Kratz, W. Paulus, D. Schumann, S. Timokhin, M. Trautmann, A. Türler, G. Wirth, A. Yakuschev, *Nature* **1997**, *388*, 55.
16. R. Eichler, W. Brüchle, R. Dressler, Ch. E. Düllmann, B. Eichler, H. W. Gäggeler, K. E. Gregorich, D. C. Hoffman, S. Hübener, D. T. Jost, U. W. Kirbach, C. A. Laue, V. M. Lavanchy, H. Nitsche, J. B. Patin, D. Piguet, M. Schädel, D. A. Shaughnessy, D. A. Strellis, S. Taut, L. Tobler, Y. S. Tsyganov, A. Türler, A. Vahle, P. A. Wilk, A. B. Yakushev, *Nature*, **2000**, *407*, 63.
17. Ch. E. Düllmann, W. Brüchle, R. Dressler, K. Eberhardt, B. Eichler, R. Eichler, H. W. Gäggler, T. N. Ginter, F. Glaus, K. E. Gregorich, D. C. Hoffman, E. Jäger, D. T. Jost, U. W. Kirbach, D. M. Lee, H. Nitsche, J. B. Patin, V. Pershina, D. Piguet, Z. Qin, M. Schädel, B. Schausten, E. Schimpf, H. –J. Schött, S. Soverna, R. Sudowe, P. Thörle, S. N. Timokhin, N. Trautmann, A. Türler, A. Vahle, G. Wirth, A. B. Yakushev, P. M. Zielinski, *Nature* **2002**, *418*, 859.
18. R. Eichler, N. V. Aksenov, A. V. Belozerov, G. A. Bozhikov, V. I. Chepigin, S. N. Dmitriev, R. Dressler, H. W. Gäggeler, V. A. Gorshkov, F. Haenssler, M. G. Itkis, A. Laube, V. Ya. Lebedev, O. N. Malyshev, Yu. Ts. Oganessian, O. V. Petrushkin, D. Piguet, P. Rasmussen, S. V. Shishkin, A. V. Shutov, A. I. Svirikhin, E. E. Tereshatov, G. K. Vostokin, M. Wegrzecki, A. V. Yeremin, *Nature*, **2007**, *447*, 72.
19. R. Eichler, N. V. Aksenov, A. V. Belozerov, G. A. Bozhikov, V. I. Chepigin, S. N. Dmitriev, R. Dressler, H. W. Gäggler, A. V. Gorshkov, M. G. Itkis, F. Haenssler, A. Laube, V. Ya. Lebedev, O. N. Malyshev, Yu. Ts. Oganessian, O. V. Petruskin, D. Piguet, A. G. Popeko, P. Rasmussen, S. V. Shishkin, A. A. Serov, A. V. Shutov, A. I. Svirikhin, E. E. Tereshatov, G. K. Vostokin, M. Wegrzecki, A. V. Yeremin, *Angew. Chem. Int. Ed.* **2008**, *47*, 3262.
20. A. Yakushev, J. M. Gates, A. Türler, M. Schädel, Ch. E. Düllmann, D. Ackermann, L. –L. Andersson, M. Block, W. Brüchle, J. Dvorak, K. Eberhardt, H. G. Essel, J. Even, U. Forsberg, A. Gorshkov, R. Graeger, K. E. Gregorich, W. Hartmann, R. –D. Herzberg, F. P. Heßberger, D. Hild, A. Hübner, E. Jäger, J. Khuyagbaatar, B. Kindler, J. V. Kratz, J. Krier, N. Kurz, B. Lommel, L. J. Niewisch, H. Nitsche, J. P. Omtvedt, E. Parr, Z. Qin, D. Rudolph, J. Runke, B. Schausten, E. Schimpf, J. Steiner, P. Thörle-Pospiech, J. Uusitalo, M. Wegrzecki, N. Wiehl, *Inorg. Chem.* **2014**, *53*, 1624.
21. M. Schädel, W. Brüchle, E. Jäger, E. Schimpf, J. V. Kratz, U. W. Scherer, H. P. Zimmermann, *Radiochim. Acta* **1989**, *48*, 171.
22. Y. Nagame, A. Toyoshima, K. Tsukada, M. Asai, T. K. Sato, M. Schädel, *J. Radioanal. Nucl. Chem.* **2014**, *300*, 77.
23. J. P. Omtvedt, J. Alstad, T. Bjørnstad, Ch. E. Düllmann, K. E. Gregorich, D. C. Hoffman, H. Nitsche, K. Opel, D. Polakova, F. Samadani, F. Schulz, G. Skarnemark, L. Stavsetra, R. Sudowe, L. Zheng, *Eur. Phys. J. D* **2007**, *45*, 91.
24. E. K. Hulet, R. W. Lougheed, J. F. Wild, J. H. Landrum, J. M. Nitschke, A. Ghiorso, *J. Inorg. Nucl. Chem.* **1980**, *42*, 79.
25. Z. Szeglowski, H. Bruchertseifer, V. P. Domanov, B. Gleisberg, L. J. Guseva, M. Hussonnois, G. S. Tikhomirova, I. Zvara, Yu. Ts. Oganessian, *Radiochim. Acta* **1990**, *51*, 71.
26. K. R. Czerwinski, K. E. Gregorich, N. J. Hannink, C. D. Kacher, B. A. Kadkhodayan, S. A. Kreek, D. M. Lee, M. J. Nurmia, A. Türler, G. T. Seaborg, D. C. Hoffman, *Radiochim. Acta* **1994**, *64*, 23.
27. K. R. Czerwinski, C. D. Kacher, K. E. Gregorich, T. M. Hamilton, N. J. Hannink, B. A. Kadkhodayan, S. A. Kreek, D. M. Lee, M. J. Nurmia, A. Türler, G. T. Seaborg, D. C. Hoffman, *Radiochim Acta* **1994**, *64*, 29.
28. A. Bilewicz, S. Siekierski, C. D. Kacher, K. E. Gregorich, D. M. Lee, N. J. Stoyer, B. Kadkhodayan, S. A. Kreek, M. R.

Lane, E. R. Sylwester, M. P. Neu, M. F. Mohar, D. C. Hoffman, *Radiochim. Acta* **1996**, *75*, 121.

29. C. D. Kacher, K. E. Gregorich, D. M. Lee, Y. Watanabe, B. Kadkhodayan, B. Wierczeinski, M. R. Lane, E. R. Sylwester, D. A. Keeney, M. Hendricks, N. J. Stoyer, J. Yang, M. Hsu, D. C. Hoffman, A. Bilewicz, *Radiochim. Acta* **1996**, *75*, 127.
30. C. D. Kacher, K. E. Gregorich, D. M. Lee, Y. Watanabe, B. Kadkhodayan, B. Wierczinski, M. R. Lane, E. R. Sylwester, D. A. Keeney, M. Hendricks, D. C. Hoffman, A. Bilewicz, *Radiochim. Acta* **1996**, *75*, 135.
31. G. Pfrepper, R. Pfrepper, D. Krauss, A. B. Yakushev, S. N. Timokhin, I. Zvara, *Radiochim. Acta* **1998**, *80*, 13.
32. D. Schumann, H. Nitsche, St. Taut, D. T. Jost, H. W. Gäggeler, A. B. Yakushev, G. V. Buklanov, V. P. Domanov, Din Thi Lien, B. Kubica, R. Misiak, A. Szeglowski, *J. Alloys Compd.* **1998**, *271–273*, 307.
33. A. Bilewicz, *J. Radioanal. Nucl. Chem.* **2001**, *247*, 407.
34. W. Brüchle, E. Jäger, V. Pershina, M. Schädel, B. Schausten, R. Günther, J. V. Kratz, W. Paulus, A. Seibert, P. Thörle, S. Zauner, D. Schumann, B. Eichler, H. Gäggeler, D. Jost, A. Türler, *J. Alloys Compd.* **1998**, *271–273*, 300.
35. R. Günther, W. Paulus, J. V. Kratz, A. Seibert, P. Thörle, S. Zauner, W. Brüchle, E. Jäger, V. Pershina, M. Schädel, B. Schausten, D. Schumann, B. Eichler, H. W. Gäggeler, D. T. Jost, A. Türler, *Radiochim. Acta* **1998**, *80*, 121.
36. E. Sturb, J. V. Kratz, A. Kronenberg, A. Nähler, P. Thörle, S. Zauner, W. Brüchle, E. Jäger, M. Schädel, B. Schausten, E. Schimpf, L. Zongwei, U. Kirbach, D. Schumann, D. Jost, A. Türler, M. Asai, Y. Nagame, M. Sakama, K. Tsukada, H. W. Gäggeler, J. P. Glatz, *Radiochim. Acta* **2000**, *88*, 265.
37. A. Kronenberg, K. Eberhardt, J. V. Kratz, P. K. Mohapatra, A. Nähler, P. Thörle, W. Brüchle, M. Schädel, A. Türler, *Radiochim. Acta* **2004**, *92*, 379.
38. J. Even, J. Ballof, W. Brüchle, R. A. Buda, Ch. E. Düllmann, K. Eberhardt, A. Gorshkov, E. Gromm, D. Hild, E. Jäger, J. Khuyagbaatar, J. V. Kratz, J. Krier, D. Liebe, M. Mendel, D. Nayak, K. Opel, J. P. Omtvedt, P. Reichert, J. Runke, A. Sabelnikov, F. Samadani, M. Schädel, B. Schausten, N. Scheid, E. Schimpf, A. Semchenkov, P. Thörle-Pospiech, A. Toyoshima, A. Türler, V. Vicente Vilas, N. Wiehl, T. Wunderlich, A. Yakushev, *Nucl. Instrum. Methods Phys. Res., Sect. A* **2011**,*638*, 157.
39. J. P. Omtvedt, J. Alstad, H. Breivik, J. E. Dyve, K. Eberhardt, C. M. Folden III, T. Ginter, K. E. Gregorich, E. A. Hult, M. Johansson, U. W. Kirbach, D. E. Lee, M. Mendel, A. Nähler, V. Ninov, L. A. Omtvedt, J. B. Patin, G. Skarnemark, L. Stavesetra, R. Sudowe, N. Wiehl, B. Wierczinski, P. A. Wilk, P. M. Zielinski, J. V. Kratz, N. Trautmann, H. Nitsche, D. C. Hoffman, *J. Nucl. Radiochem. Soc.* **2002**, *3*, 121.
40. H. Haba, K. Tsukada, M. Asai, S. Goto, A. Toyoshima, I. Nishinaka, K. Akiyama, M. Hirata, S. Ichikawa, Y. Nagame, Y. Shoji, M. Shigekawa, T. Koike, M. Iwasaki, A. Shinohara, T. Kaneko, T. Maruyama, S. Ono, H. Kudo, Y. Oura, K. Sueki, H. Nakahara, M. Sakama, A. Yokoyama, J. V. Kratz, M. Schädel, W. Brüchle, *J. Nucl. Radiochem. Sci.* **2002**, *3*, 143.
41. H. Haba, K. Tsukada, M. Asai, A. Toyoshima, Y. Ishii, H. Toume, T. Sato, I. Nishinaka, T. Ichikawa, S. Ichikawa, Y. Nagame, W. Sato, K. Matsuo, Y. Kitamoto, Y. Tashiro, A. Shinohara, J. Saito, M. Ito, T. Ikezawa, M. Sakamaki, S. Goto, H. Kudo, H. Kikunaga, M. Arai, S. Kamataki, A. Yokoyama, K. Akiyama, K. Sueki, Y. Oura, M. Schädel, W. Brüchle, J. V. Kratz, *Radiochim. Acta* **2007**, *95*, 1.
42. A. Toyoshima, Y. Kasamatsu, K. Tsukada, M. Asai, Y. Ishii, H. Toume, I. Nishinaka, T. K. Sato, Y. Nagame, M. Schädel, H. Haba, S. Goto, H. Kudo, K. Akiyama, Y. Oura, K. Ooe, A. Shinohara, K. Sueki, J. V. Kratz, *J. Nucl. Radiochem. Sci.* **2010**, *11*, 7.
43. H. Haba, K. Tsukada, M. Asai, A. Toyoshima, K. Akiyama, I, Nishinaka, M. Hirata, T. Yaita, S. Ichikawa, Y. Nagame, K. Yasuda, Y. Miyamoto, T. Kaneko, S. Goto, S. Ono, T. Hirai, H. Kudo, M. Shigekawa, A. Shinohara, Y. Oura, H. Nakahara, K. Sueki, H. Kikunaga, N. Kinoshita, N. Tsuruga, A. Yokoyama, M. Sakama, S. Enomoto, M. Schädel, W. Brüchle, J. V. Kratz, *J. Am. Chem. Sci.* **2004**, *126*, 5219.
44. A. Toyoshima, H. Haba, K. Tsukada, M. Asai, K. Akiyama, I. Nishinaka, Y. Nagame, D. Saika, K. Matsuo, W. Sato, A. Shinohara, H. Ishizu, M. Ito, J. Saito, S. Goto, H. Kudo, H. Kikunaga, N. Kinoshita, C. Kato, A. Yokoyama, K. Sueki, *J. Nucl. Radiochem. Sci.* **2004**, *5*, 45.
45. A. Toyoshima, H. Haba, K. Tsukada, M. Asai, K. Akiyama, S. Goto, Y. Ishii, I. Nishinaka, T. K. Sato, Y. Nagame, W. Sato, Y. Tani, H. Hasegawa, K. Matsuo, D. Saika, Y. Kitamoto, A. Shinohara, M. Ito, J. Saito, H. Kudo, A. Yokoyama, M. Sakama, K. Sueki, Y. Oura, H. Nakahara, M. Schädel, W. Brüchle, J. V. Kratz, *Radiochim. Acta* **2008**, *96*, 125.
46. Y. Ishii, A. Toyoshima, K. Tsukada, M. Asai, H. Toume, I. Nishinaka, Y. Nagame, S. Miyashita, T. Mori, H. Suganuma, H. Haba, M. Sakamaki, S. Goto, H. Kudo, K. Akiyama, Y. Oura, H. Nakahara, Y. Tashiro, A. Shinohara, M. Schädel, W. Brüchle, V. Pershina, J. V. Kratz, *Chem. Lett.* **2008**, *37*, 288.
47. Y. Ishii, A. Toyoshima, K. Tsukada, M. Asai, Z. Li, Y. Nagame, S. Miyashita, T. Mori, H. Suganuma, H. Haba, S. Goto, H. Kudo, K. Akiyama, Y. Oura, A. Shinohara, M. Schädel, V. Pershina, J. V. Kratz, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 903.
48. Z. J. Li, A. Toyoshima, M. Asai, K. Tsukada, T. K. Sato, N. Sato, T. Kikuchi, Y. Nagame, M. Schädel, V. Pershina, X. H. Liang, Y. Kasamatsu, Y. Komori, K. Ooe, A. Shinohara, S. Goto, H. Murayama, M. Murakami, H. Kudo, H. Haba, Y. Takeda, M. Nishikawa, A. Yokoyama, S. Ikarashi, K. Sueki, K. Akiyama, J. V. Kratz, *Radiochim. Acta* **2012**, *100*, 157.
49. V. Pershina, D. Trubert, C. Le Naour, J. V. Kratz, *Radiochim Acta* **2002**, *90*, 869.
50. V. Pershina, D. Polakova, J. P. Omtvedt, *Radiochim. Acta* **2006**, *94*, 407.
51. J. V. Kratz, H. P. Zimmermann, U. W. Scherer, M. Schädel, W. Brüchle, K. E. Gregorich, C. M. Gannett, H. L. Hall, R. A. Henderson, D. M. Lee, J. D. Leyba, M. J. Nurmia, D. C. Hoffman, H. Gäggeler, D. Jost, U. Baltensperger, Ya Nai-Qi, A. Türler, Ch. Lienert, *Radiochim. Acta* **1989**, *48*, 121.
52. H. P. Zimmermann, M. K. Gober, J. V. Kratz, M. Schädel, W. Brüchle, E. Schimpf, K. E. Gregorich, A. Türler, K. R. Czerwinski, N. J. Hannink, B. Kadkhodayan, D. M. Lee, M. J. Nurmia, D. C. Hoffman, H. Gäggeler, D. Jost, J. Kovacs, U. W. Scherer, A. Weber, *Radiochim. Acta* **1993**, *60*, 11.
53. M. K. Gober, J. V. Kratz, H. P. Zimmermann, M. Schädel, W. Brüchle, E. Schimpf, K. E. Gregorich, A. Türler, N. J. Hannink, K. R. Czerwinski, B. Kadkhodayan, D. M. Lee, M. J. Nurmia, H. Gäggeler, D. Jost, J. Kovacs, U. W. Scherer, A. Weber, *Radiochim. Acta* **1992**, *57*, 77.

54. M. Schädel, W. Brüchle, E. Schimpf, H. P. Zimmermann, M. K. Gober, J. V. Kratz, N. Trautmann, H. Gäggeler, D. Jost, J. Kovacs, U. W. Scherer, A. Weber, K. E. Gregorich, A. Türler, K. R. Czerwinski, N. J. Hannink, B. Kadkhodayan, D. M. Lee, M. J. Nurmia, D. C. Hoffman, *Radiochim. Acta* **1992**, *57*, 85.
55. D. Trubert, C. Le Naour, F. Monroy Guzman, M. Hussonnois, L. Brillard, J. F. Le Du, O. Constantinescu, J. Gasparro, V. Barci, B. Weiss, G. Ardisson, *Radiochim. Acta* **2002**, *90*, 127.
56. W. Paulus, J. V. Kratz, E. Strub, S. Zauner, W. Brüchle, V. Pershina, M. Schädel, B. Schausten, J. L. Adams, K. E. Gregorich, D. C. Hoffman, M. R. Lane, C. Laue, D. M. Lee, C. A. McGrath, D. K. Shaughnessy, D. A. Strellis, E. R. Sylwester, *J. Alloys Compd.* **1998**, *271-273*, 292.
57. W. Paulus, J. V. Kratz, E. Strub, S. Zauner, W. Brüchle, V. Pershina, M. Schädel, B. Schausten, J. L. Adams, K. E. Gregorich, D. C. Hoffman, M. R. Lane, C. Laue, D. M. Lee, C. A. McGrath, D. K. Shaughnessy, D. A. Strellis, E. R. Sylwester, *Radiochim. Acta* **1999**, *84,* 69.
58. K. Tsukada, H. Haba, M. Asai, A. Toyoshima, K. Akiyama, Y. Kasamatsu, I, Nishinaka, S. Ichikawa, K. Yasuda, Y. Miyamato, K. Hashimoto, Y. Nagame, S. Goto, H. Kudo, W. Sato, A. Shinohara, Y. Oura, K. Sueki, H. Kikunaga, N. Kinoshita, A. Yokoyama, M. Schädel, W. Brüchle, J. V. Kratz, *Radiochim. Acta* **2009**, *97,* 83.
59. Y. Kasamatsu, A. Toyoshima, M. Asai, K. Tsukada, Z. Li, Y. Ishii, H. Toume, T. K. Sato, T. Kikuchi, I. Nishinaka, Y. Nagame, H. Haba, H. Kikunaga, Y. Kudou, Y. Oura, K. Akiyama, W. Sato, K. Ooe, H. Fujisawa, A. Shinohara, S. Goto, T. Hasegawa, H. Kudo, T. Nanri, M. Araki, N. Kinoshita, A. Yokoyama, F. Fan, Z. Qin, Ch. E. Düllmann, M. Schädel, J. V. Kratz, *Chem. Lett.* **2009**, *38*, 1084.
60. H. Haba, Y. Kasamatsu, H. Kikunaga, A. Yoneda, J. Kanaya, K. Morita, *RIKEN Accel. Prog. Rep.* **2012**, *45*, 204.
61. Y. Kasamatsu, A. Kino, T. Yokokita, K. Nakamura, Y. Komori, K. Toyomura, T. Yoshimura, H. Haba, J. Kanaya, M. Huang, Y. Kudou, N. Takahashi, A. Shinohara, *Radiochim. Acta* in press.
62. A. Kino, Master's thesis of Graduate School of Science, Osaka University **2013** in Japanese.
63. Z. Zhu, C. Y. Chen, *Hydrometallurgy* **2011**, *107*, 1.
64. E. H. Huffman, G. M. Iddings, R. C. Lilly, *J. Am. Chem. Soc.* **1951**, 73, 4474.
65. G. W. Leddicotte, F. L. Moore, *J. Am. Chem. Soc.* **1952**, *74*, 1618.
66. J. Y. Ellenburg, G. W. Leddocptte, F. L. Moore, *Anal. Chem.* **1954**, 26, 1045.
67. A. M. Wilson, L. Churchill, K. Kiluk, P. Hovesepian, *Anal. Chem.* **1962**, 34, 203.
68. H. Marchart, F. Hecht, *Mikrochim. Acta* **1962**, 1152.
69. T. B. Pierce, W. M. Henry, *J. Chromatog.* **1966**, *23*, 457.
70. F. G. Seeley, D. J. Crouse, *J. Chem. Eng. Data* **1966**, *11*, 424.
71. N. R. Das, S. Lahiri, *Anal. Sci.* **1992**, *8*, 317.
72. T. Omori, N. Suzuki, *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1633.
73. L. R. Bunney, N. E. Ballou, J. Pascual, S. Foti, *Anal. Chem.* **1959**, *31*, 324.
74. L. Wish, *Anal. Chem.* **1959**, *31*, 326.
75. T. Sato, S. Kikuchi, *Z. Anorg. Allg. Chem.* **1969**, *365*, 330.
76. F. L. Moore, *Anal. Chem.* **1958**, *30*, 908.
77. Y. Kasamatsu, A. Toyoshima, H. Toume, K. Tsukada, H. Haba, Y. Nagame, *J. Nucl. Radiochem. Sci.* **2007**, *8*, 69.
78. X. H. Liang, K. Tsukada,, A. Toyoshima, Z. J. Li, M. Asai, T. K. Sato, N. Sato, Y. Nagame, *J. Radioanal. Nucl. Chem.* **2012**, *292*, 917.
79. A. Kino, Y. Kasamatsu, T. Yokokita, T. Yoshimura, Y. Komori, Y. Kikutani, N. Takahashi, A. Shinohara, *Solvent Extr. Res. Dev. Jpn.* in press.
80. H. Haba, K. Akiyama, K. Tsukada, M. Asai, A. Toyoshima, T. Yaita, M. Hirata, K. Sueki, Y. Nagame, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 698.
81. Ch. E. Düllmann, A. Türler, *Phys. Rev. C* **2008**, *77*, 064320.
82. M. Asai, K. Tuskada, M. Sakama, S. Ichikawa, Y. Ishii, Y. Nagame, I. Nishinaka, K. Akiyama, A. Osa, Y. Oura, K. Sueki, M. Shibata, *Phys. Rev. Lett.* **2005**, *95*, 102502.
83. O. L. Keller, A. Chetham-Strode, *Inorg. Chem.* **1966**, *5*, 367.
84. W. P. Griffith, T. D. Wickins, *J. Chem. Soc. (A)* **1967**, 675.
85. J. L. Kim, H. Lagally, H. J. Born, *Anal. Chim. Acta.* **1973**, *64*, 29.
86. Y. Kasamatsu, A. Toyoshima, H. Haba, H. Toume, K. Tsukada, K. Akiyama, T. Yoshimura, Y. Nagame, *J. Radioanal. Nucl. Chem.* **2009**, *279*, 371.
87. D. Trubert, C. Le Naour, C. Jaussaud, *J. Sol. Chem.* **2002**, *31*, 261.
88. G. H. Morrison, H. Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley and Sons, Inc, New York, **1957**.
89. R. Kurin, R. J. Myers, *J. Physical and Colloid Chem.* **1947**, *51*, 1111.
90. F. Nelson, T. Murase, K. Kurt, A. Kraus, *J. Chromatog.* **1964**, *13*, 503.
91. B. Kubica, M. Tuteja-Krysa, Szeqlowski, *J. Radioanal. Nucl. Chem.* **1999**, *242*, 541.
92. J. H. Kanzelmeyer, J. Ryan, H. Freund, *J. Am. Chem. Soc.* **1956**, *78*, 3020.
93. J. E. D. Davies, D. A. Lomg, *J. Chem. Soc. (A)* **1968**, 2560.
94. *The Chemistry of the Actinide and Transactinide Elements*, 3rd edn. Vol. 1. ed. By R. Moress, M. Edelstein, J. Fuger, J. J. Katz, Springer, Dordrecht, **2006**.
95. G. A. Welch, *Nature* **1953**, *172*, 458.
96. C. Le Naour, M. V. Di Giandomenico, Y. Mendes, *Radiochim. Acta* **2009**, *97*, 361.
97. J. Shanker, K. S. Venkateswarlu, C. Gopinathan, *J. Inorg. Nucl. Chem.* **1963**, *25*, 57.
98. A. T. Casey, A. G. Maddock, *J. Inorg. Nucl. Chem.* **1959**, *10*, 289.
99. K. A. Kurt, G. E. Moore, *J. Am. Chem. Soc.* **1950**, *72*, 4293.
100. H. J. Ding, Y. N. Niu, Y. B. Xu, W. F. Yang, S. G. Yuan, Z. Qin, X. L. Wu, *J. Radioanal. Nucl. Chem.* **2007**, *272*, 263.

101. A. G. Goble, A. G. Maddock, *J. Inorg. Nucl. Chem.* **1958**, *7*, 94.
102. M. Mendes, J. Aupiais, C. Jutier, F. Pointurier, *Anal. Chim. Acta* **2013**, *780*, 110.
103. R. D. Shannon, *Acta Cryst* **1976**, *A32*, 751.
104. Y. Kasamatsu, A. Toyoshima, H. Toume, K. Tsukada, M. Asai, H. Haba, Y. Nagame, *J. Nucl. Radiochem. Sci.* **2013**, *13*, 9.
105. H. J. Ding, Y. N. Niu, Y. B. Xu, S. G. Yuan, X. H. Zhou, *J. Radioanal. Nucl. Chem.* **2006**, *268*, 433.
106. H. Haba, M. Huang, D. Kaji, J. Kanaya, Y. Kudou, K. Morimoto, M. Murakami, K. Ozeki, R. Sakai, T. Sumita, Y. Kasamatsu, Y. Kikutani, Y. Komori, K. Nakamura, A. Shinohara, H. Kikunaga, H. Kudo, K. Nishio, A. Toyoshima, K. Tsukada, *Phys. Rev. C* **2014**, *89*, 024618.
107. V. Pershina, *Radiochim. Acta* **1998**, *80*, 75.
108. H. Haba, D. Kaji, H. Kikunaga, Y. Kudou, K. Morimoto, K. Morita, K. Ozeki, T. Sumita, A. Yoneda, Y. Kasamatsu, Y. Komori, K. Ooe, A. Shinohara, *Phys. Rev. C* **2011**, *83*, 034602.
109. R. J. Silva, W. J. McDowell, O. L. Keller, J. R. Tarrant, *Inorg. Chem.* **1974**, *13*, 2233.
110. W. Brüchle, *Radiochim. Acta* **2003**, *91*, 71.
111. N. Sato, T. K. Sato, M. Asai, A. Toyoshima, K. Tsukada, Z. J. Li, K. Nishio, Y. Nagame, M. Schädel, H. Haba, S. Ichikawa, H. Kikunaga, *Radiochim. Acta* **2014**, *102*, 211.
112. A. Toyoshima, Y. Kasamatsu, K. Tsukada, M. Asai, Y. Kitatsuji, Y. Ishii, I. Nishinaka, H. Haba, K. Ooe, W. Sato, A. Shinohara, K. Akiyama, Y. Nagame, *Electrochemical studies of the heaviest actinides*, Seventh workshop on the chemistry of the heaviest elements, Mainz, October, **2009**.
113. T. Sikkeland, A. Ghiorso, M. J. Nurmia, *Phys. Rev.* **1968**, *172*, 1232.

Appendix 1. Liquid-Liquid Extraction Behaviors of Zr and Hf from HCl into Aliquat 336 Carbon Tetrachloride Solution

A1.1 Introduction

To search for rapid extraction system, liquid-liquid extraction of Zr and Hf in the Alqiuat 336/HCl system was also performed.

A1.2 Experimental

A1.2.1 Liquid-Liquid Extraction Using Aliquat 336

Equal volumes of 6–11 M HCl (aqueous solutions) and 0.1 M Aliquat 336-carbontetrachloride (organic solutions) were mixed in the PP tube, and the tube was shaken using a shaker at 25 ± 1 ºC for longer than 30 min. After the centrifugation of the mixture, the aqueous and organic phases were individually pipetted into different tubes and used in the following liquid-liquid extraction experiment.

The 1 mL of the aqueous solution containing ^{88}Zr or ^{175}Hf tracer solutions were in a PP tube was mixed with 1 mL of the organic solution. Then the mixture was shaken at 25 ± 1 ºC for 10s–90min using the shaker. After 1-min centrifugation, a certain volume of both the phases were precisely pipetted into separate tubes, and the samples were subjected to γ-ray measurement using a Ge detector.

The *D* values were evaluated by the following equation:

$$D = \frac{A_{\mathrm{org}} V_{\mathrm{aq}}}{A_{\mathrm{aq}} V_{\mathrm{org}}} . \qquad \text{(A1-1)}$$

The subscripts “aq” and “org” denotes the aqueous and organic phases, respectively.

To examine the time required to equilibrium in the liquid-liquid extraction reactions, the time dependences of the *D* values of Zr and Hf were studied in the range 10s–90min under following condition. With 0.01 M Aliquat 336, the HCl concentrations of 7.7 and 10.6 M for Zr and 7.6 and 10.7 M for Hf were used. Based on these results, the *D* values of Zr and Hf in equilibria were determined in various HCl concentrations with shaking time of 90 min. The HCl concentrations in the range 6.3–10.7 M were used.

A1.3 Results and Discussion

A1.3.1 Dependence of Distribution Ratio on Shaking Time

The dependences of the *D* values of Zr and Hf on the shaking time in the extraction with 0.01 M Aliquat 336 are shown in Figure A1-1(a) and (b), respectively. The *D* values of Zr and Hf become constant after 10–20 min in 7.6 M HCl for Zr and 7.7 M HCl for Hf, suggesting that the chemical reactions in the extraction reach equilibrium within 20 min. The *D* values of these elements were almost constant in the time range 10s–90min in 10.6 M HCl for Zr and 10.7 M HCl for Hf, indicating that the extraction reactions equilibrated within 10 s. From these results, extraction kinetics is rapid in high concentration of HCl. On the other hand, the extraction reaction in the solid-liquid extraction reached equilibrium within 10 s in all the HCl concentration studied in Subsection 2.1.3. Extraction reaction is shortened, and/or a more rapid extraction system mighte still be required.

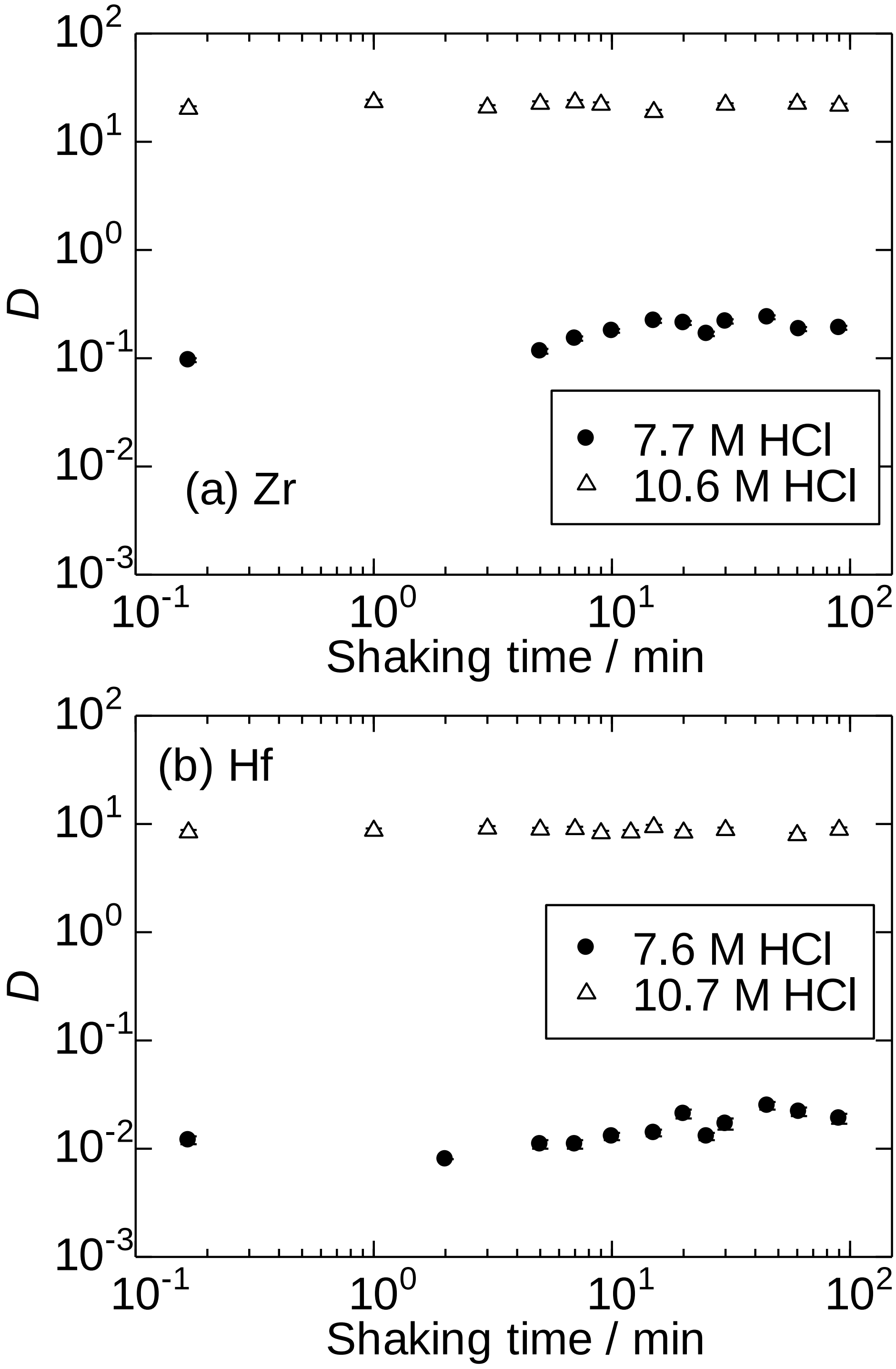


Figure. A1-1. The *D* values of (a) Zr and (b) Hf for different shaking times in various HCl concentrations with 0.01 M Aliquat 336 in carbon tetrachloride solution.

A1.3.2 Dependence of Distribution Ratio on HCl Concentration

The dependence of the the *D* values of Zr and Hf on the HCl concentration in the extraction with 0.01 M Aliquat 336 are shown in Figure A1-2. The *D* values of these elements were increased with an increase HCl concentration, indicating that Zr and Hf formed anionic chloride complexes. The *D* values of Zr were higher than those of Hf in this condition. These extraction behaviors were consistent with those in the solid-liquid extraction in Subsection 2.1.3.

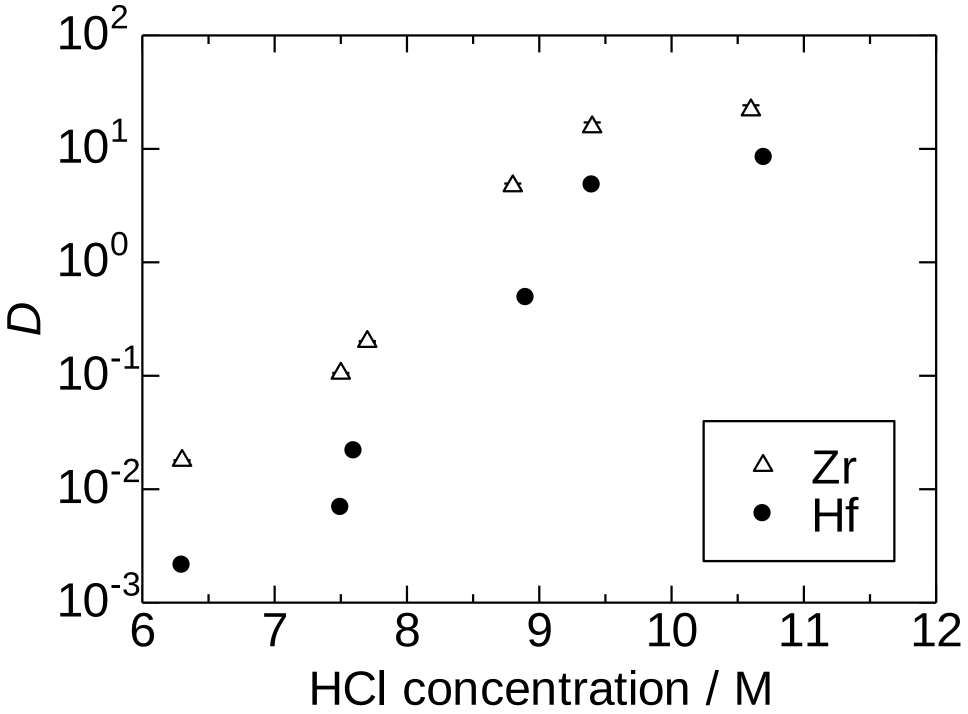


Figure A1-2. The *D* values of Zr and Hf as a function of HCl concentration with 0.01 M Aliquat 336 in carbon tetrachloride solution.

Appendix 2. Liquid-Liquid Extraction Behaviors of Nb, Ta, and Pa from HCl into Aliquat 336 Carbon Tetrachloride Solution

A2.1 Introduction

To search for rapid extraction system, liquid-liquid extraction of Nb, Ta, and Pa in the Alqiuat 336/HCl system was also performed.

A2.2 Experimental

A2.2.1 Adsorption on Polypropylene Surface

To study adsorption of Nb, Ta, and Pa on the surface of the PP tube in liquid-liquid extraction, following experiment was carried out. Equal volumes of 0.1–11 M HCl (aqueous solutions) and 9.1×10^{-6}–0.10 M Aliquat 336-carbon tetrachloride (organic solutions) were mixed in the PP tube, and the tube was mechanically shaken using a mixer at 25 ± 1 °C for longer than 30 min. After the centrifugation of the mixture, the aqueous and organic phases were individually pipetted into different tubes and used in the following liquid-liquid extraction experiment.

The1 mL of the aqueous solution containing ^{95}Nb, ^{177,179}Ta, or ^{233}Pa tracer solutions were mixed with 1 mL of the organic solution. Then the mixture was shaken at 25 ± 1 °C for 10s–4h using the shaker. After 1-min centrifugation, 0.85 mL of both the phases was pipetted into separate tubes, and the samples were subjected to γ-ray measurement using a Ge detector.

Standard samples for Nb, Ta, or Pa in 0.1, 1, 5, and 11 M HCl with the same geometry (0.85 mL) were also prepared. These solutions were subjected to γ- or X-ray measurement using a Ge detector. The adsorption ratios (*S*) of Nb, Ta, and Pa on the surface of the PP tubes were determined by the following equation.

$$S = \frac{A_{\mathrm{aq}} + A_{\mathrm{org}}}{A_0} \quad . \qquad \text{(A2-1)}$$

No adsorption indicates $S = 1$, while 100% adsorption corresponds to $S = 0$.

The time dependences of the S values of Nb, Ta, and Pa were studied in the range 10s–4h under following condition. With 0.1 M Aliquat 336, the HCl concentrations of 0.26, 5.9, 7.6, and 10.1 M for Nb, 0.18, 4.7, 6.4, 8.1, and 10.5 M for Ta, and 0.24, 4.1, 7.1, and 9.7 M for Pa were used.

A2.2.2 Liquid-Liquid Extraction Using Aliquat 336

The experimental procedures are the same as those described in the Subsection A2.2.1. The *D* value was evaluated by the equation (A1-1).

To examine the time required to equilibrium in the liquid-liquid extractions, the time dependences of the *D* values of Nb, Ta, and Pa were studied in the range 10s–4h under following condition. With 0.01 M Aliquat 336, the HCl concentrations of 0.12, 3.4, 5.3, 6.6, 7.2, 8.5, 9.6, and 10.1 M for Nb, 0.18, 4.3, 5.8, 8.1, and 11.0 M for Ta, and 0.18, 4.2, 5.3, and 10.3 M for Pa were used. With 0.1 M Aliquat 336, the HCl concentrations of 0.26, 2.4, 4.1, 7.6, 8.3, 9.1, 9.7, and 10.1 M for Nb, 0.18, 4.7, 5.5, 6.4, 8.0, and 10.5 M for Ta, and 0.24, 4.1, 7.1, and 9.7 M for Pa were used. Based on these results, the *D* values in equilibria were determined in various HCl and Aliquat 336 concentrations with shaking time of 1.5 h for Nb and Pa or 4 h for Ta. The HCl concentrations in the range 0.12–11.0 M were used in the extraction with 0.01 M Aliquat 336, while the HCl concentrations in the range 0.18–10.6 M were used in the extraction with 0.1 M Aliquat 336. In addition, the HCl concentration was kept constant at 6, 8, and 10 M HCl, and the Aliquat 336 concentration was varied for 9.1×10^{-6}–0.10 M.

A2.3 Results and Discussion

A2.3.1 Adsorption on Polypropylene Surface

The dependences of the *S* values of Nb, Ta, and Pa on the shaking time are shown in Figure A2-1(a)–(c), respectively. For all the elements, the *S* values were constant at ~1 under all the conditions studied, which suggests that almost all of the Nb, Ta, and Pa species in the aqueous and organic phases do not adsorb on the surface of the PP tubes. As a result, it is evident that influence of the adsorption of the group 5 elements on the PP surfaces is negligible in the present cation-exchange and extraction experiments, which indicates that the accurate *D* values of Nb, Ta, and Pa were examined in this experiment.

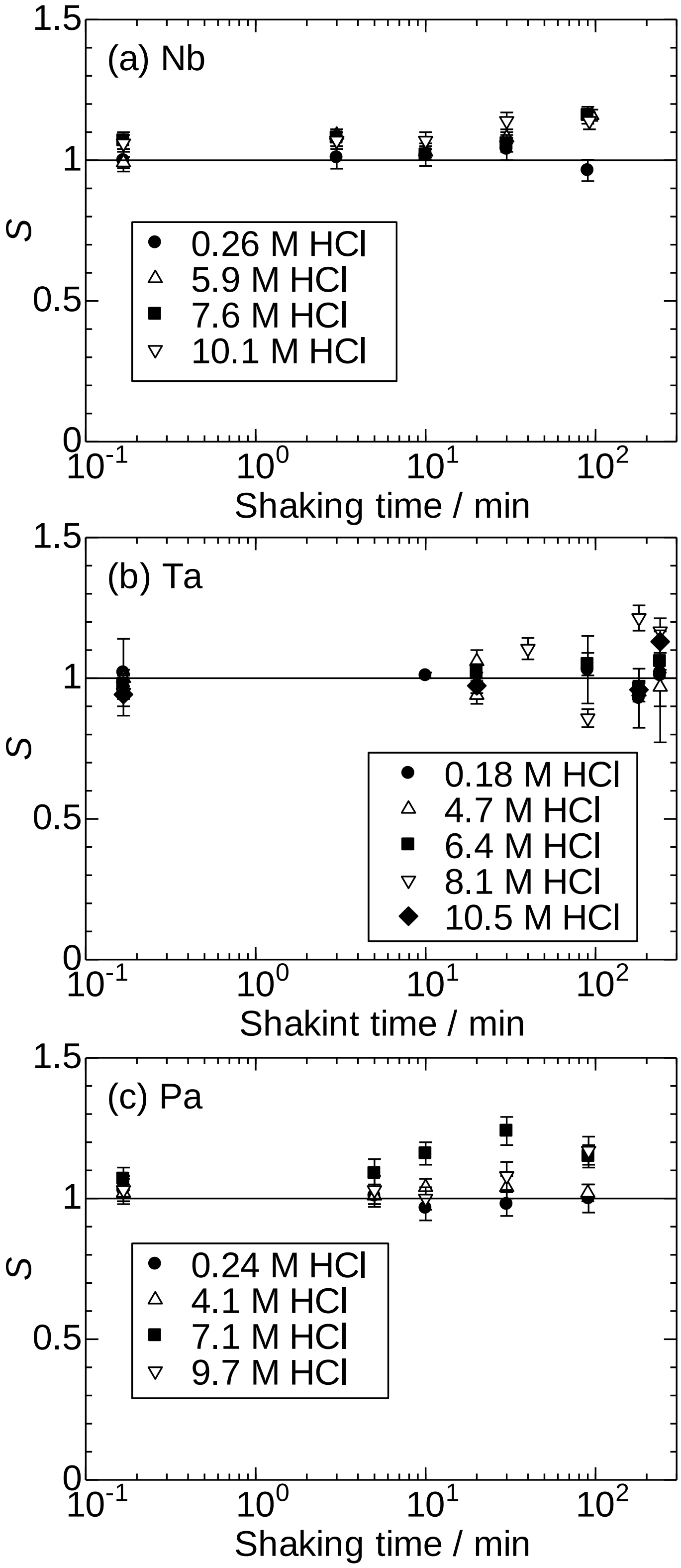


Figure A2-1. The *S* values of (a) Nb, (b) Ta, and (c) Pa for different shaking times in various HCl concentrations with 0.1 M Aliquat 336 in carbon tetrachloride solution. As such, no adsorption corresponds to *S* =1 (horizontal line), while 100% adsorption indicated by *S* = 0.

A2.3.2 Dependence of Distribution Ratio on Shaking Time

The dependences of the *D* values of Nb, Ta, and Pa on the shaking time in the extraction with 0.01 M Aliquat 336 are shown in Figure A2-3(a)–(c), respectively; the corresponding data with 0.1 M Aliquat 336 are shown in Figure A2-3(d)–(f). The *D* values of Nb were constant in the time range 10s–135min, indicating that the extraction equilibrium was accomplished within 10 s of shaking in 0.12–10.1 M HCl. The *D* values of Ta became constant after 2–3 h in all of the HCl concentrations. The *D* values of Pa were constant in 10s–110min except in the 0.01 M Aliquat 336/10.3 M HCl system. In the liquid-liquid extraction as well as solid-liquid extraction in Subsection 2.2.3, the reaction kinetics of Ta was also slower than that of Nb and Pa.

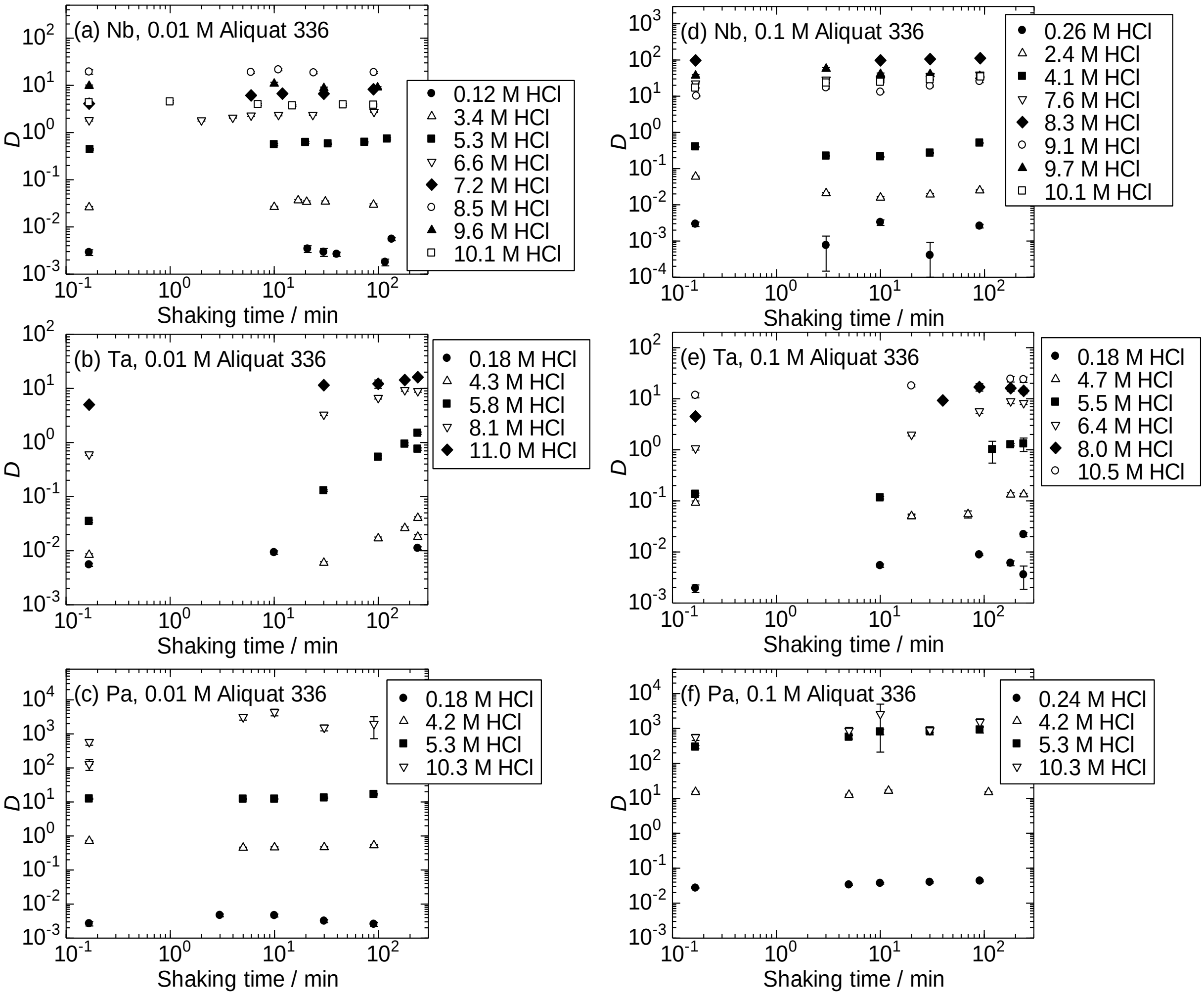


Figure A2-2. The *D* values of (a), (d) Nb, (b), (e) Ta, and (c), (f) Pa for different shaking times in various HCl concentrations with (a)–(c) 0.01 M and (d)–(f) 0.1 M Aliquat 336 in carbon tetrachloride solution.

A2.3.3 Dependence of Distribution Ratio on HCl Concentration

The dependences of the *D* values of Nb, Ta, and Pa on the HCl concentration in the extraction with 0.01 M and 0.1 M Aliquat 336 are shown in Figures A2-3(a) and (b), respectively. Lower *D* values for Nb at HCl concentrations lower than 4 M indicate low concentration of the anionic Nb species at these values.

The *D* values of Nb, Ta, and Pa increased with an increase HCl concentration, indicating that the formation of the anionic species. These extraction behaviors were consistent with those in the solid-liquid extraction in Subsection 2.2.3.

The *D* values for the Aliquat 336 extractions were found to be Pa > Ta ≥ Nb. The *D* values of Nb did not decrease for high concentrations of HCl for the 0.1 M Aliquat 336 experiment. This suggests that ion-pair with Aliquat 336 cation and protonation of anionic Nb complexes competes (anionic species of Nb is formed ion-pair with Aliquat 336 cation in high concentration of Aliquat 336 and protonation species in low concentration of Aliquat 336).

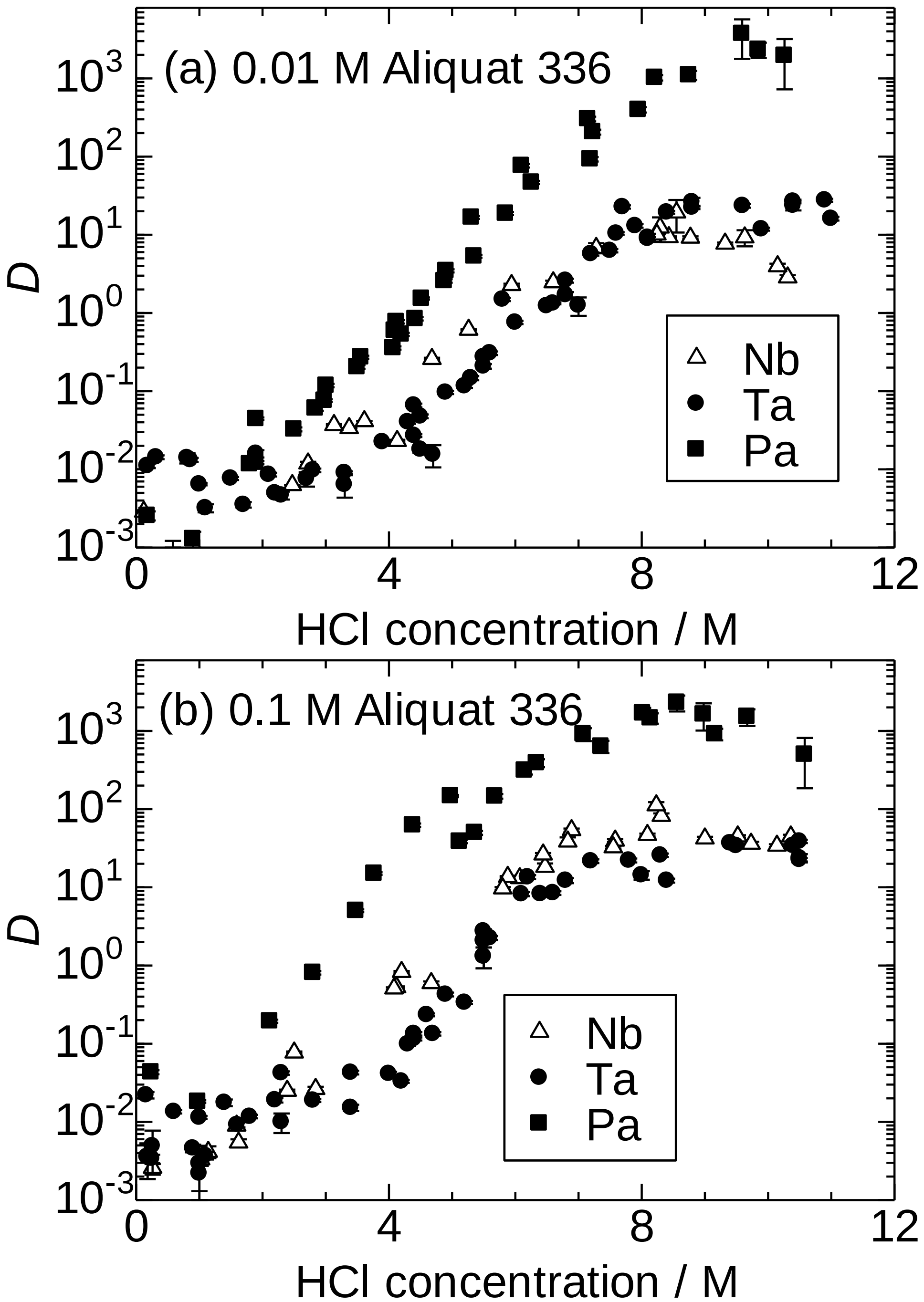


Figure A2-3. The *D* values of Nb, Ta, and Pa as a function of the HCl concentration with (a) 0.01 M and (b) 0.1 M Aliquat 336 in carbon tetrachloride solution.

A2.3.4 Dependence of Distribution Ratio on Aliquat 336 Concentration

The relationship between *D* values and the concentration of Aliquat 336 was investigated to evaluate the net charge of the extracted anionic metal complexes. In the extraction from 6, 8, and 10 M HCl, the dependence of the log *D* on the log [Aliquat 336] are shown in Figure A2-4(a)–(c), respectively. The log *D* values of all the Nb samples linearly increased with increasing log [Aliquat 336]. For Ta, the linear relationships between log *D* and log [Aliquat 336] values were obtained in 6 M HCl, 8 M HCl (for $-4.7 \leq$ log [Aliquat 336] ≤ -3.0), and 10 M HCl (for $-5.0 \leq$ log [Aliquat 336] ≤ -3.0). For Pa, the linear relationships between log *D* and log [Aliquat 336] values were obtained in 6 M HCl, 8 M HCl, and 10 M HCl (for $-4.9 \leq$ log [Aliquat 336] ≤ -3.2). All available slopes are summarized in Table A2-1.

The slope values for Nb under all conditions are approximately 1, which indicates that the net charges of the extracted metal complexes are −1 in 6, 8, and 10 M HCl. As such, $[Nb(OH)_2Cl_4]^-$ [72,85,92] and/or $[NbOCl_4]^-$ [85] are the likely chemical species.

All Ta experiments for which linear slopes were obtained gave values of approximately 1, which also indicates that the anionic Ta complex has a net charge of −1, such as $[TaCl_6]^-$.[84,93] Note that the *D* values of Ta were higher than those of Nb for log [Aliquat 336] ≤ -2 in 8 and 10 M HCl.

Finally, slope values for Pa in the 6 and 8 M HCl liquid-liquid extraction were approximately 1. This again indicates an anionic complex with a net charge of −1, such as $[Pa(OH)_2Cl_4]^-$, $[Pa(OH)Cl_5]^-$, $[PaCl_6]^-$,[97–99] and/or $[PaOCl_4]^-$.[100] Meanwhile, the slope value in the 10 M HCl ($-4.9 \leq$ log [Aliquat 336] ≤ -3.2) liquid-liquid extraction was about 2, which indicates an anionic Pa complex with a net charge of −2, such as $[PaCl_7]^{2-}$ [94,97] and/or $[PaOCl_5]^{2-}$.[94]

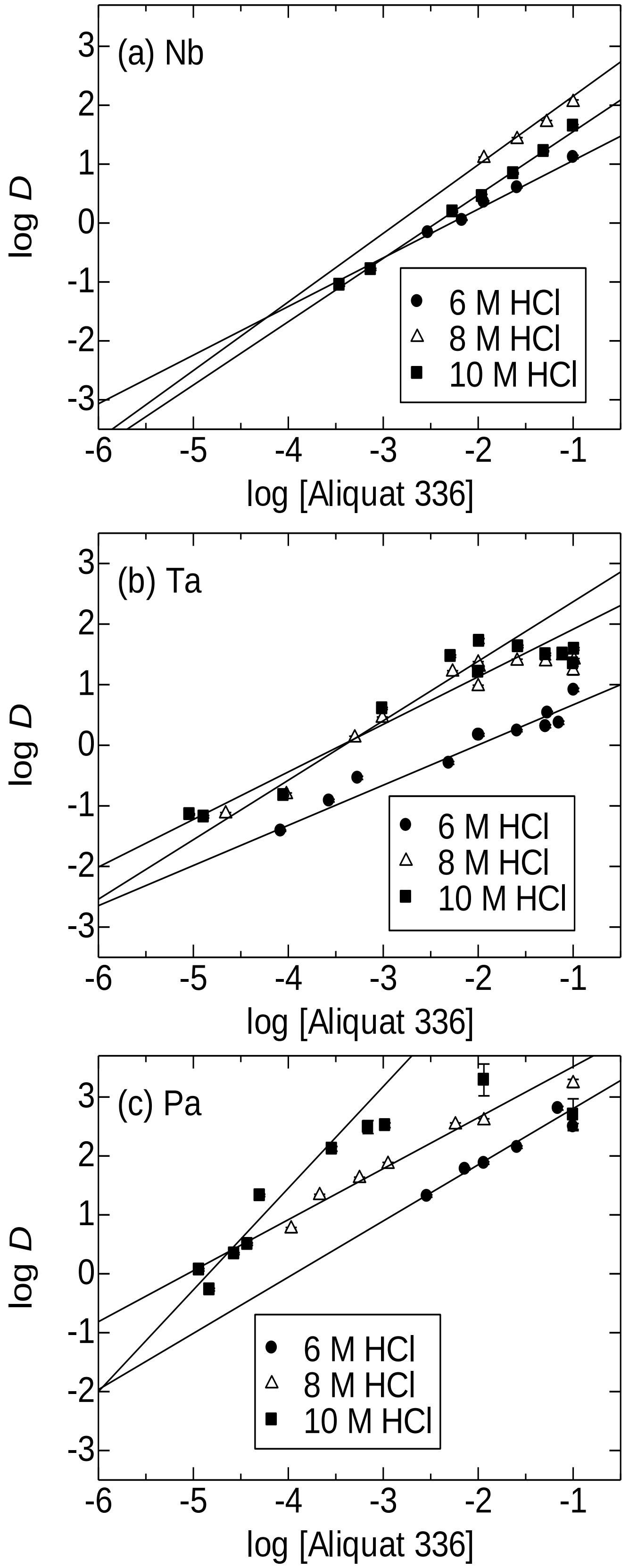


Figure A2-4. The *D* values of (a) Nb, (b) Ta, and (c) Pa as a function of Aliquat 336 concentration at the constant HCl concentration of 6, 8, and 10 M.

Table A2-1. Slopes (*s*) of linear lines in Fig. A2-4: log *D* = *s* log [Aliquat 336] + *C*

HCl concentration / M	Slope (*s*)								
	Nb			Ta			Pa		
6	0.8	±	0.1	0.7	±	0.1	1.0	±	0.1
8	1.2	±	0.1	1.0	±	0.1[a]	0.9	±	0.1
10	1.1	±	0.1	0.8	±	0.1[b]	1.7	±	0.1[c]

[a] $-4.66 \leq \log$ [Aliquat 336] ≤ -3.01 ; b: $-5.04 \leq \log$ [Aliquat 336] ≤ -3.01 ; c: $-4.94 \leq \log$ [Aliquat 336] ≤ -3.16.

Appendix 3. Elution Curve

A3.1 Experimental

The ^{89g,m}Zr and ^{173}Hf nuclides were produced using the AVF cyclotron at RCNP (Subsection 3.2.3). The reaction products were transported by the He/KCl gas-jet system. The transported products were deposited on a collection site on a slider in dissolution equipment, ASO, for 60 s. Subsequently, the deposited sample was dissolved in 8.9 M HCl at a flow rate 1 mL min^{-1}. The solution sample was collected below ASO and the slider of batch-type solid-liquid extraction apparatus, AMBER.

A3.2. Results

Figures A3-1 show elution curves of ^{89g}Zr and ^{173}Hf in the 8.9 M HCl, and the solution sample was collected below (a) ASO and (b) the slider of AMBER. The nuclides were accomplished elution within 6 and 12 s below ASO and the slider of AMBER, respectively..

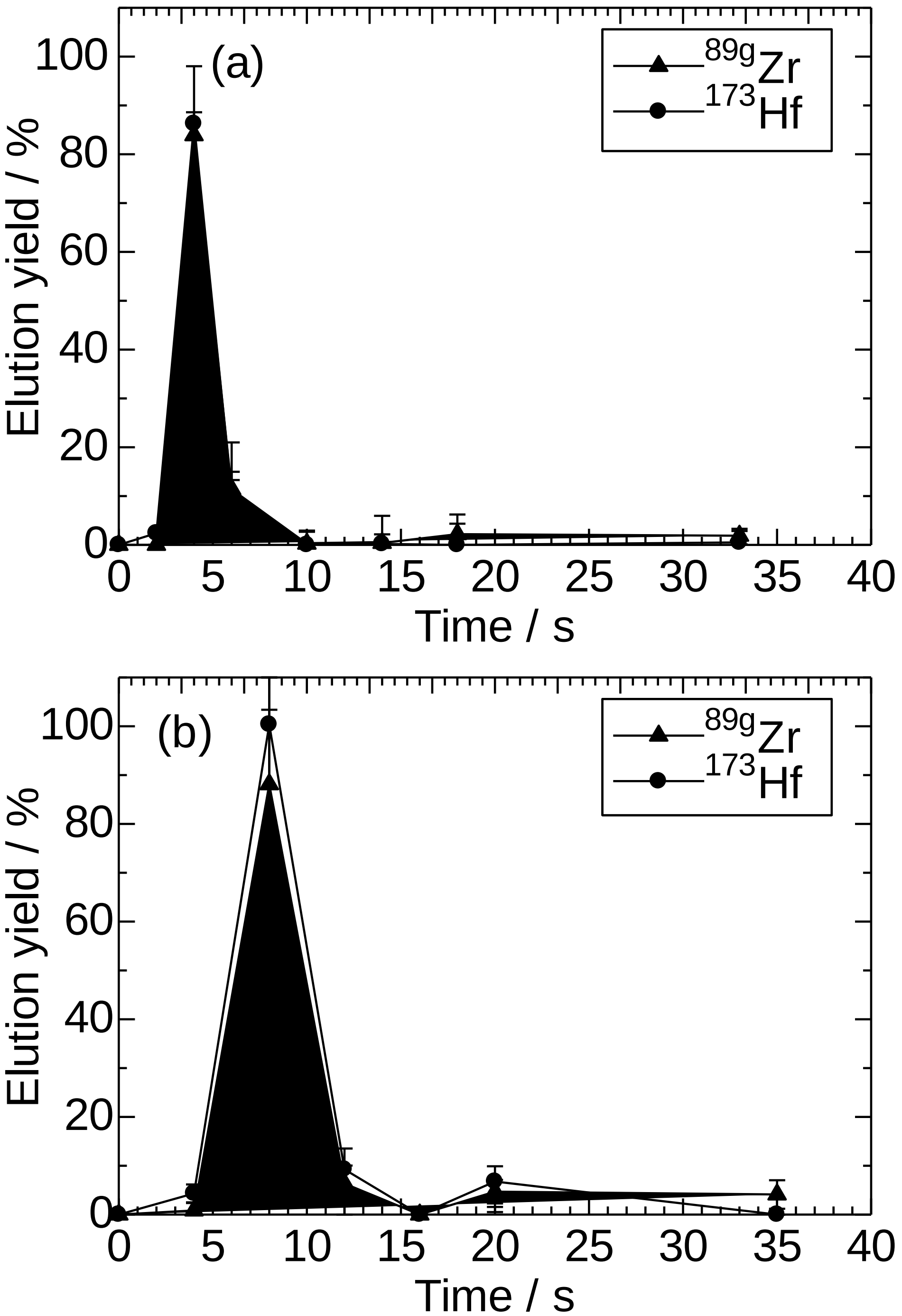


Figure A3-1. Elution curves of ^{89g}Zr and ^{173}Hf in 8.9 M HCl at a flow rate of 1 mL min^{-1}. (a) Solution sample was corrected below ASO and (b) below the slider of AMBER.

List of Publications

Main publication

1. T. Yokokita, Y. Kasamatsu, T. Yoshimura, N. Takahashi, A. Shinohara
   Distribution behaviors of Nb, Ta, and Pa as homologues of Db in cation exchange and solid-liquid and liquid-liquid extractions by Aliquat 336 from hydrochloric acid
   Solvent Extr. Ion Exch. submitted.
2. Y. Kasamatsu, A. Kino, T. Yokokita, K. Nakamura, Y. Komori, K. Toyomura, T. Yoshimura, H. Haba, J. Kanaya, M. Huang, Y. Kudou, N. Takahashi, A. Shinohara
   Development of an automated batch-type solid-liquid extraction apparatus and extraction of Zr, Hf, and Th by triisooctylamine from HCl solutions for chemistry of element 104, Rf
   Radiochim. Acta in press.

Other publication

1. T. Yokokita, K. Ooe, Y. Kasamatsu, T. Yoshimura, N. Takahashi, N. Shiohara, K. Takamiya, Y. Komori, Y. Kikutani, A. Kino, A. Shinohara
   Solvent extraction using carrier-free radiotracers of Mo and W from HCl and HCl/LiCl solutions into Aliquat 336
   J. Radioanal. Nucl. Chem. **2015**, *303*, 1091.
2. T. Yokokita, Y. Kasamatsu, K. Ooe, T. Yoshimura, N. Takahashi, Y. Komori, A. Shinohara
   Solvent extraction of Mo(V) and Mo(VI) from hydrochloric acid into Aliquat 336 chloroform solution
   J. Radioanal. Nucl. Chem. **2014**, *301*, 751.
3. A. Kino, Y. Kasamatsu, T. Yokokita, T. Yoshimura, Y. Komori, Y. Kikutani, N. Takahashi, A. Shinohara
   Solvent extraction of zirconium and hafnium as homologues of rutherfordium by triisooctylamine from HCl solutions
   Solvent Extr. Res. Dev. Jpn. in press
4. Y. Komori, T. Yokokita, Y. Kasamatsu, H. Haba, A. Toyoshima, K. Toyomura, K. Nakamura, J. Kanaya, M. Huang, Y. Kudou, N. Takahashi, A. Shinohara
   Solid-liquid extraction of Mo and W by Aliquat 336 from HCl solutions toward extraction chromatography experiments of Sg
   J. Radioanal. Nucl. Chem., **2015**, *303*, 1385.
5. K. Ooe, M. F. Attallah, M. Asai, N. Goto, N. S. Gupta, H. Haba, M. Huang, J. Kanaya, Y. Kaneya, Y. Kasamatsu, Y. Kitatsuji, Y. Kitayama, K. Koga, Y. Komori, T. Koyama, J. V. Kratz, H. V. Lerum, S. Miyashita, Y. Oshimi, V. Pershina, D. Sato, T. K. Sato, Y. Shigekawa, A. Shinohara, A. Tanaka, A. Toyoshima, K. Tsukada, S. Tsuto, T. Yokokita, A. Yokoyama, J. P. Omtvedt, Y. Nagame, M. Schädel
   Development of a new continuous dissolution apparatus with a hydrophobic membrane for superheavy element chemistry
   J. Radioanal. Nucl. Chem., **2015**, *303*, 1317.
6. S. Ueno, K. Toda, A. Asano, N. Takahashi, Y. Kasamatsu, T. Yokokita, A. Yokoyama
   Measurement of evaporation-residue cross sections with light beams and deformed lanthanide target nuclei
   J. Radioanal. Nucl. Chem., **2015**, 303, 1273.
7. A. Toyoshima, K. Ooe, S. Miyashita, M. Asai, M. F. Attallah, N. Goto, N. S. Gupta, H. Haba, M. Huang, J. Kanaya, Y. Kaneya, Y. Kasamatsu, Y. Kitatsuji, Y. Kitayama, K. Koga, Y. Komori, T. Koyama, J. V. Kratz, H. V. Lerum, Y. Oshimi, V. Pershina, D. Sato, T. K. Sato, Y. Shigekawa, A. Shinohara, A. Tanaka, K. Tsukada, S. Tsuto, T. Yokokita, A. Yokoyama, J. P. Omtvedt, Y. Nagame, and M. Schädel
   Chemical studies of Mo and W in preparation of a seaborgium (Sg) reduction experiment using MDG, FEC, and SISAK
   J. Radioanal. Nucl. Chem., **2015**, *303*, 1169.
8. Y. Kasamatsu, K. Toyomura, N. Shiohara, T. Yokokita, Y. Komori, A. Kino, T. Yoshimura, N. Takahashi, H. Haba, Y. Kudou, H. Kikunaga, T. Mitsugashira, T. Ohtsuki, K. Takamiya, A. Shinohara
   Coprecipitation behaviors of Zr, Hf, and Th with Sm hydroxide for chemical study of element 104, Rf
   J. Nucl. Radiochem. Sci., **2014**, *14*, 7.
9. Y. Kasamatsu, Y. Kikutani, A. Kino, Y. Komori, T. Yokokita, T. Yoshimura, N. Takahashi, A. Shinohara
   Solvent extraction of Zr and Hf from hydrochloric acid using tributylphosphate for the extraction of element 104, rutherfordium
   Radiochim. Acta **2013**, *101*, 515.