Electronic Supplement Information

Observation of the chemical reaction equilibria of element 104, rutherfordium: Solid-liquid extraction of Rf, Zr, Hf and Th with Aliquat 336 resin from HCl

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Contents

1. The procedures used in offline solid-liquid extraction of ^{88}Zr, ^{175}Hf and ^{234}Th

The isotopes ^{88}Zr ($t_{1/2}$ = 83.4 d)[1] and ^{175}Hf ($t_{1/2}$ = 70 d)[1] were produced by the bombardment of ^{89}Y and ^{nat}Lu targets (300–400 mg cm^{-2}), respectively, with ^{1}H beams (an energy of 22 MeV for Zr and 14 MeV for Hf; a beam current of 1–2 μA) at the AVF cyclotron located at RCNP. The isotope ^{234}Th ($t_{1/2}$ = 24.10 d)[1] was obtained as an α decay daughter nuclide of ^{238}U ($t_{1/2}$ = 4.468 × 10^{9} y)[1]. The isotopes were purified by anion-exchange chromatography and solvent extraction.[2]

MCI GEL CHP20/P30 (Mitsubishi Chemical Corporation) was used as an inert resin to support Aliquat 336. The 28 wt% Aliquat 336 resin was prepared in a similar manner to that described in ref. 2 using Aliquat 336 purchased from Sigma-Aldrich. The 28 wt% Aliquat 336 resin (0.57–15 mg) and 6–11 M HCl (0.25 mL) containing the isotopes ^{88}Zr, ^{175}Hf and ^{234}Th were mixed in the polypropylene (PP) tubes, and were shaken at 25 ± 1 °C for 10s–1d using the shaker. After 1-min centrifugation using centrifugal PP filter units (Ultrafree-Cl), the resin was separated from the solution phase. The solution phase was then subjected to γ-ray measurement using a Ge detector. Control experiments without the resin were also performed.

To study the time required to reach equilibrium in the extraction, we investigated the time dependences of the Q_d values of these elements in various HCl concentrations (6.5, 8.7 and 10.9 M for Zr and Hf; 6.6 and 11.3 M for Th). Based on these results, the K_d values of these elements were determined at various HCl concentrations (6.5–11.3 M) with shaking times ≥ 4 h. Finally, the concentrations of the HCl solutions were determined by titration with a standardized NaOH solution.

2. The dependence of the Q_d values on shaking time in the offline experiment

Figs. S1a, S1b and S1c show the dependences of the Q_d values of ^{88}Zr, ^{175}Hf and ^{234}Th, respectively, on shaking time in the offline solid-liquid extraction. Overall, the Q_d values of these elements were constant throughout the time ranges studied, indicating that the extraction equilibrium of these elements was accomplished within 10 s, whereas the contact time between the two phases was longer than 1 min in the manual batch method due to the centrifugation for phase separation. In any case, we found the extraction reactions of Zr, Hf and Th in the Aliquat336/HCl system to be fast and suitable for application to the online experiment.

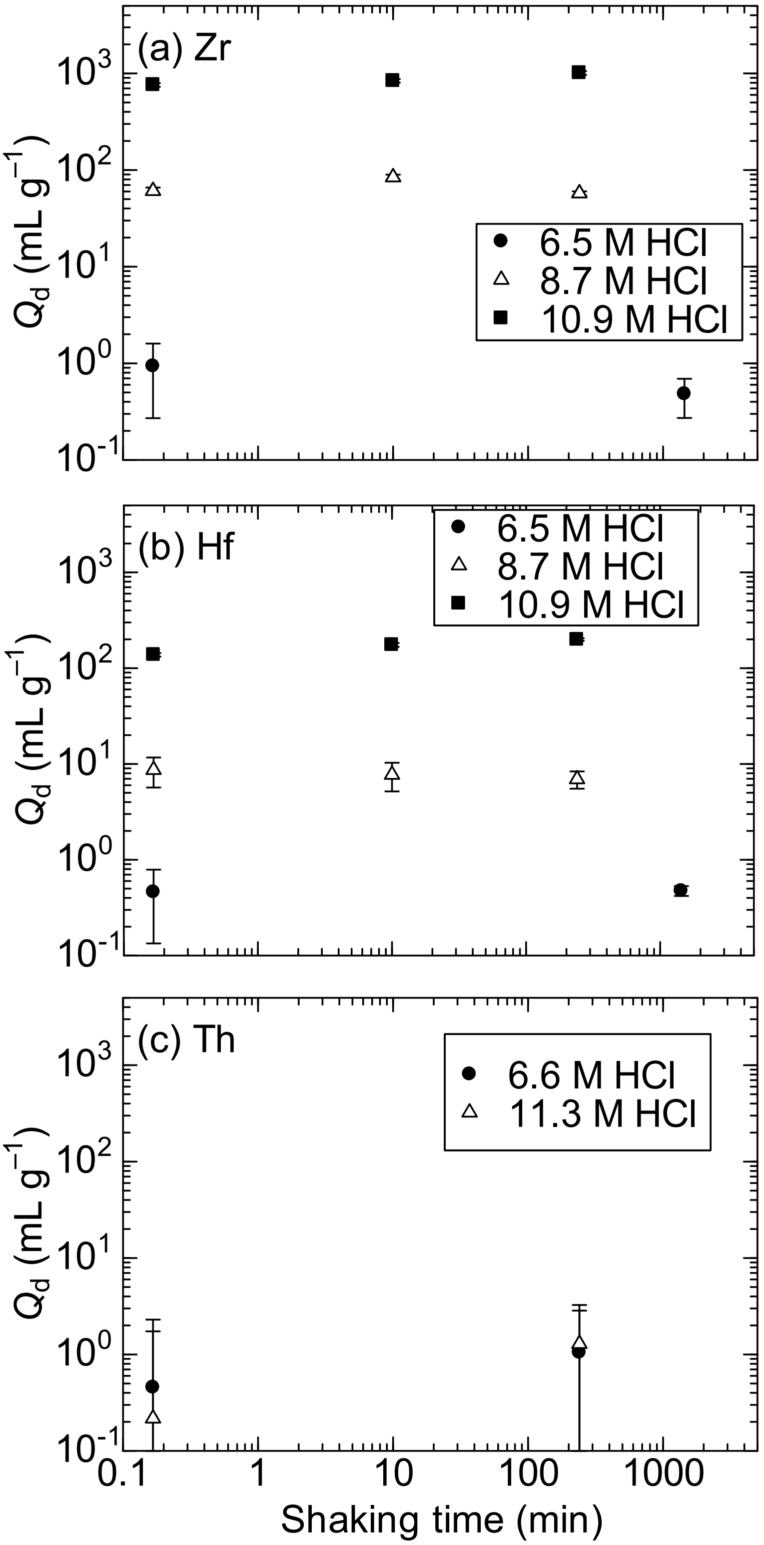

Fig. S1. Q_d values of (a) Zr, (b) Hf and (c) Th as a function of shaking time in extraction from HCl with 28 wt% Aliquat 336 resin.

3. The procedures used in online solid-liquid extraction of $^{89g,m}Zr$ and ^{173}Hf

The isotopes ^{89g,m}Zr ($t_{1/2}$ = 78.41 h, 4.18 min)[1] and ^{173}Hf ($t_{1/2}$ = 23.6 h)[1] were simultaneously produced by the bombardment of 1 sheet of ^{nat}SrO and 4 sheets of $^{nat}Yb_2O_3$ electrodeposited targets on Al backing foil (3 μm) with ^{4}He beams (an energy of 40 MeV and a beam current approximately 1.3 μA) at the AVF cyclotron located at RCNP. The product isotopes that were recoiling out of the targets were attached to KCl particles in He gas (about 135 kPa) and transported to a chemistry laboratory by an He gas stream at a flow rate of 2.5 L min^{-1}. The transported products were deposited on the AMBER's dissolution equipment for 60, 133 and 153 s. After collection, the products were dissolved with 8.2, 9.2, 10.3 and 11.2 M HCl (approximately 0.23 mL), and the solution sample was injected into the solid-liquid extraction container containing the 28 wt% Aliquat 336 resin (1.7–3.8 mg). After shaking at 27 ± 1 °C for 10, 30 and 120 s, only the solution phase was expelled from the container by compressed air (about 0.15 MPa) for 10 s. The eluent was collected in a PP tube. We then stripped the Zr and Hf species adsorbed on the resin by washing the resin three times with 3.9 M HCl (0.3 mL) with 5-s shaking, and each solution was collected in a PP tube. We then measured the γ-ray activities of all the collected solution samples. Subsequently, the resin was conditioned with HCl (0.16 mL) with 2-s shaking for the next extraction. Control experiments without the resin were also performed. The chemical yields of ^{89g,m}Zr and ^{173}Hf were both approximately 55%.

To study the time required to reach equilibrium in the extraction, we investigated the time dependences of the Q_d values of Zr and Hf in 9.2 and 11.2 M HCl. Based on these results, the K_d values of both elements were determined in 8.2 and 10.3 M HCl with 10-s shaking.

4. The data in repetitive use of Aliquat 336 and TIOA resins

We performed repetitive solid-liquid extractions of ^{88}Zr and ^{175}Hf with 28 wt% Aliquat 336 and 31 wt% TIOA resins from 10 M HCl using AMBER. Figs. S2a and S2b show the K_d values of these elements using 28 wt% Aliquat 336 and 31 wt% TIOA resins as a function of the number of cycles, respectively. Gamma-ray measurements were performed for some of the samples and all the obtained data are presented in these figures. Herein, we define two methods for evaluating the K_d value: the control method and the 2-solution method.[2] In the control method, the radioactivity in the resin phase is determined by subtracting the radioactivity in the solution phase from that in the control solution ($A_\mathrm{r} = A_\mathrm{c} - A_\mathrm{s}$). In the 2-solution method, the radioactivity in the resin phase, A_r, is determined by measuring the radioactivity in the stripping solution.

The K_d values of both elements with 28 wt% Aliquat 336 resin were constant in all the experiments performed, indicating that constant K_d values can be obtained in 102 repetitive extractions without renewing the resin. On the other hand, the K_d values obtained with 31 wt% TIOA resin decreased with an increased number of cycles, and the resin had to be renewed every 5 times. In the solid-liquid extraction with TIOA resin, 6 M HNO_3/0.01 M HF was required for stripping (the adsorbed Zr and Hf species on the TIOA resin could not be stripped by 4 M HCl),[2] and this is probably the reason for the decreasing K_d values. Based on these results, we employed 28 wt% Aliquat 336 resin for the Rf experiment.

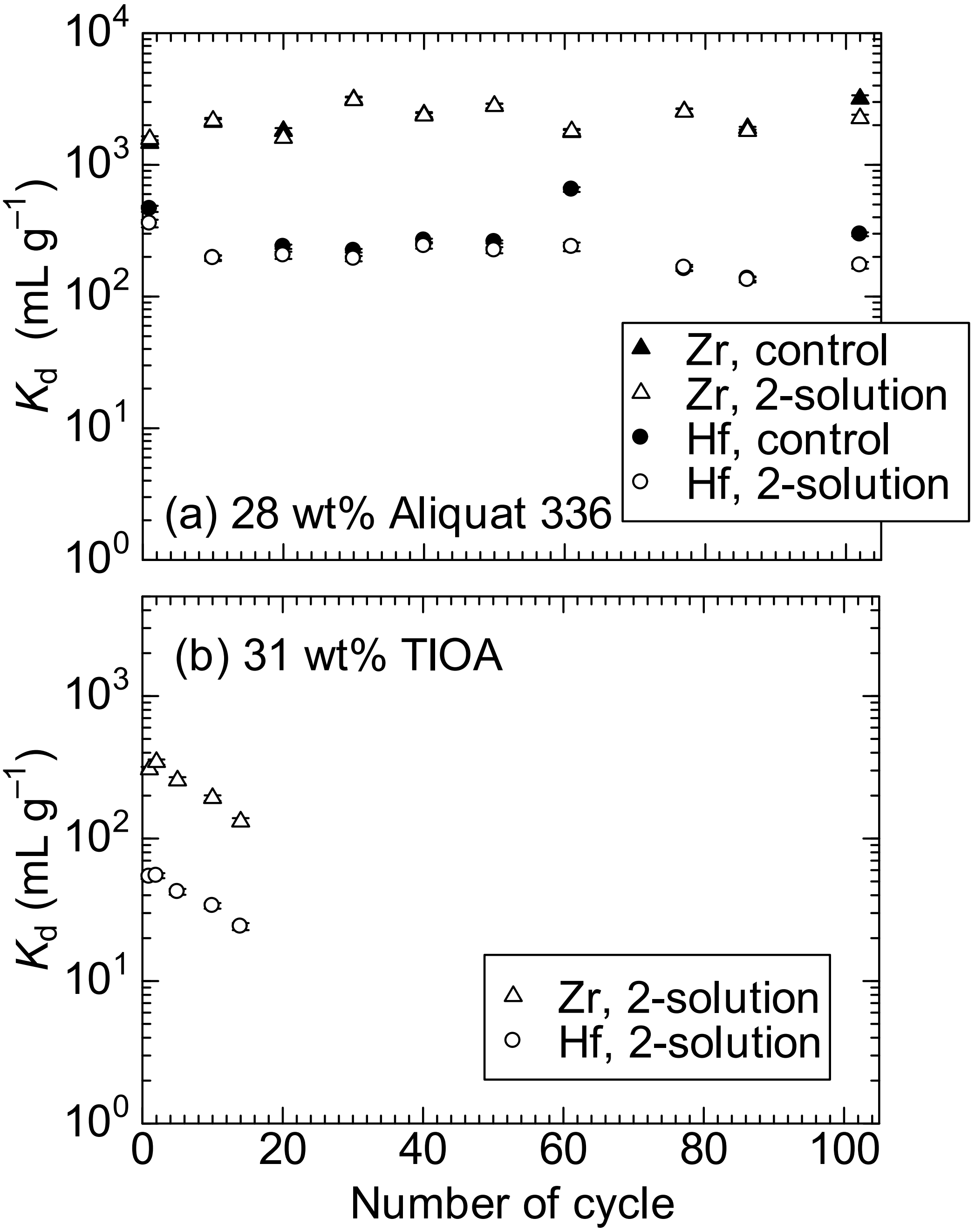

Fig. S2. K_d values of Zr and Hf as a function of the number of cycles in extraction from 10 M HCl with (a) 28 wt% Aliquat 336 and (b) 31 wt% TIOA resins.

5. The K_d values determined by control method and 2-solution method in the online experiment

Fig. S3 shows the dependences of the K_d values of ^{89g}Zr and ^{173}Hf on the HCl concentration in the solid-liquid extraction with 28 wt% Aliquat 336 resin by the control and 2-solution methods. The K_d values evaluated by the control method were consistent with those found by the 2-solution method, suggesting that the K_d values in the present reaction system can be obtained by either method when using AMBER.

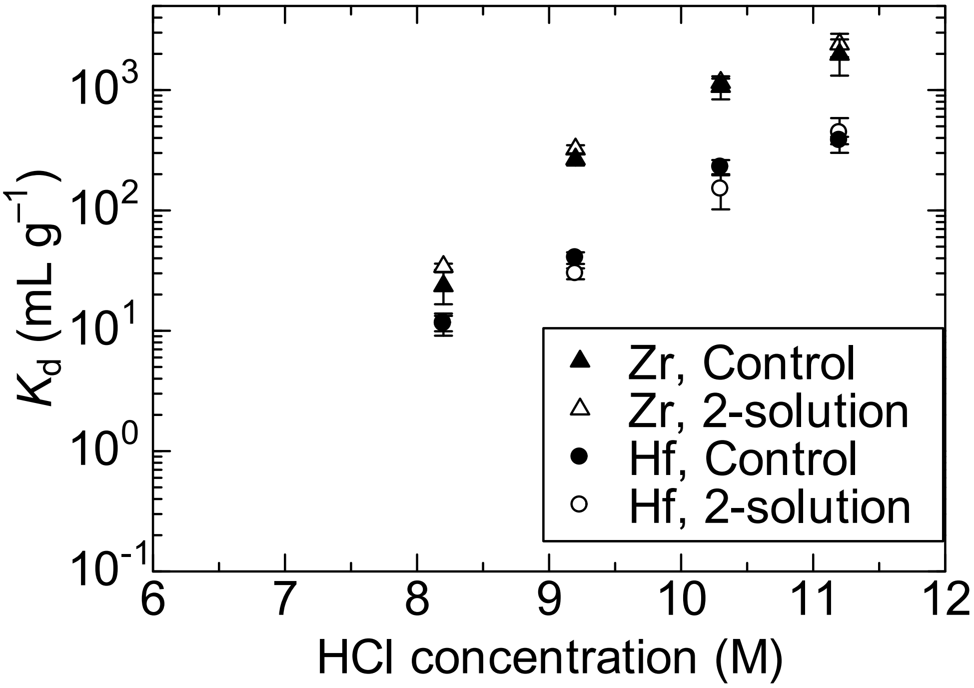

Fig. S3. K_d values of Zr and Hf as a function of HCl concentration in extraction with 28 wt% Aliquat 336 resin.

6. Supporting results from the Rf experiment

Figs. S4a and S4b show the typical α spectra of samples prepared in a control experiment with 10-s shaking (7.9 and 9.0 M HCl; 71 cycles) and a solid-liquid extraction experiment with 10-s shaking (7.9 M HCl; 38 cycles), respectively. We observed α peaks for ^{150}Dy (E_α = 4.23 MeV), ^{151}Dy (E_α = 4.07 MeV), ^{248}Cm (E_α = 5.39 and 5.34 MeV), ^{244}Cm (E_α = 5.80 and 5.76 MeV) and ^{254}Fm (E_α = 7.19 and 7.15 MeV). From the energy resolutions of these peaks, we defined an energy range from 7.91 to 8.43 MeV for the α counts of the ^{261}Rf (E_α = 8.28 MeV) and its daughter ^{257}No (E_α = 8.22, 8.32 MeV).

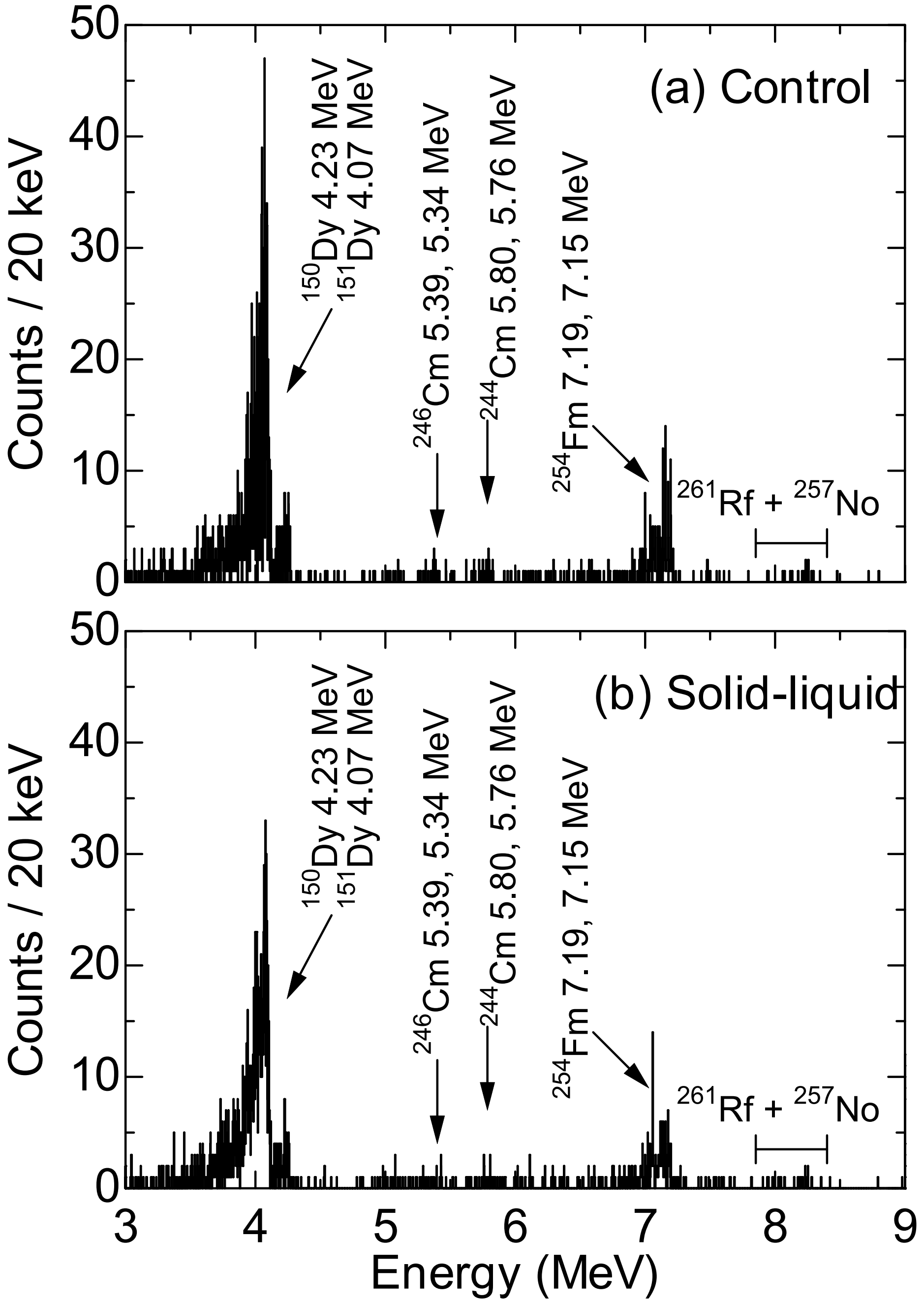

Fig. S4. Alpha-particle spectra observed in (a) the control experiment without resin in 7.9 M HCl with 10-s shaking (37 cycles) and (b) the solid-liquid extraction experiment with 28 wt% Aliquat 336 resin in 9.0 M HCl with 10-s shaking (38 cycles).

The results of the control experiments are summarized in Table S1, which shows the HCl concentration, shaking time, total ^{18}O beam dose, number of cycles of the extraction, chemical yield determined by ^{169}Hf radioactivity measurements, number of observed α particles and the ratio of total α events to α–α correlations. The corresponding data for the solid-liquid extraction experiments are shown in Table S2.

The calculated α/α–α ratios were estimated on the basis of the standard growth and decay of ^{261}Rf and ^{257}No, detection efficiency (34%) and time intervals in the extraction, evaporation and α-particle measurement. The time intervals in all runs were registered. As mentioned in the text, we assumed in this estimation that the No^{2+} ion does not adsorb on the Aliquat 336 resin. The asymmetric errors of the observed α/α–α ratios were evaluated based on the 68% confidence intervals for Poisson distributed values.[3] The chemical yield of ^{169}Hf in the solid-liquid extraction was determined from the radioactivity in the solution phase only, considering the amount of Hf species extracted with 28 wt% Aliquat 336 resin (15% in 9 M HCl).

Table S1. Summary of online experiments of Rf in the control experiment without resin

[HCl]	Shaking time	Total beam dose	Number of cycle of the experiment	Average chemical yield of ^{169}Hf	α-count		α/α-α	
(M)	(s)	$\times 10^{17}$		(%)	α	α-α	experiment	calculation
7.9	10	0.649	37	42	19	2	$9.0^{+19.0}_{-4.3}$	7.3
9.0	10	0.588	34	49	19	5	$3.8^{+3.0}_{-1.4}$	7.2
9.0	30	0.786	47	29	12	2	$6.0^{+12.0}_{-2.8}$	7.3

Table S2. Summary of online experiments of Rf in the solid-liquid extraction experiment with 28 wt% Aliquat 336 resin

[HCl]	Shaking time	Total beam dose	Number of cycle of the experiment	Average chemical yield of ^{169}Hf	α-count		α/α-α	
(M)	(s)	$\times 10^{17}$		(%)	α	α-α	experiment	calculation
7.9	10	0.679	38	56	24	6	$4.0^{+2.7}_{-1.4}$	7.3
7.9	30	0.849	50	52	21	3	$7.0^{+9.3}_{-2.8}$	7.4
7.9	60	1.842	105	43	34	5	$6.8^{+5.4}_{-2.3}$	7.6
9.0	10	1.201	68	47	3	0	–	14.0

[a] The chemical yield of ^{169}Hf was corrected with a 15% extraction of the Hf species with 28 wt% Aliquat 336 resin.

References

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